SURFACE ENHANCED RAMAN SCATTERING (SERS) STUDIES OF SOME PYRIDINE DERIVATIVES

ABSTRCAT

THESIS

SUBMITTED FOR THE DEGREE OF

Doctor of Philosophy

IN

PHYSICS

BY

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DEPARTMENT OF PHYSICS
ALIGARH MUSLIM UNIVERSITY
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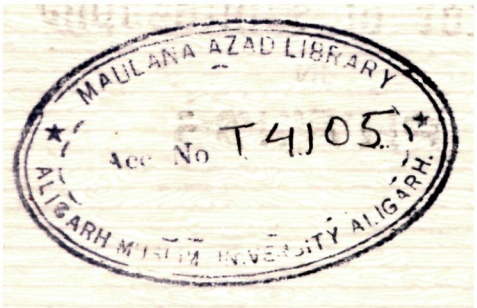
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ABSTRACT

Raman spectroscopy is an important technique for chemical analysis because of its excellent capability of chemical group identification. The Raman process itself -- inelastic light scattering by molecular vibrations -- is inherently very weak. Only a small fraction, 10^{-6} or so, of the photons incident on a sample are Raman scattered. Thus a major limitation of the conventional Raman method is its low sensitivity. Recently, the Raman technique has enjoyed an increased interest among the spectroscopists following the observation of enormous Raman enhancement for some molecules adsorbed on special metal surfaces. There are certain molecules which when adsorbed on specially prepared metal surfaces or on metal colloids exhibits inordinate Raman signals whose intensity is $\approx 10^{2}$ - 10^{6} times larger than the normal Raman signals. This enormous increase in Raman signal arises from a surface enhancement process and the phenomenon has been termed as Surface Enhanced Raman Scattering (SERS).

In the present investigation, the surface-enhanced Raman scattering (SERS) of some pyridine derivatives viz. 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 2-chloropyridine, 3-chloropyridine, 2-aminopyridine, 2-cyanopyridine and 4-cyanopyridine have been studied using silver sol technique. The thesis comprises of nine chapters.

The First Chapter is a general introduction to the SERS. A brief discussion on the discovery of SERS, nature of SERS and scope of SERS have been presented. SERS was first discovered in pyridine molecules adsorbed on roughened silver electrode. Afterwards, investigations are being carried on with different molecules with different metal-electrodes, colloidal solutions, silver membranes etc. After analyzing the results of all experiments on SERS, it has been widely accepted that the surface roughness is a prerequisite for SER effect. The dependence of the SERS enhancement on surface roughness exhibits different excitation profile for different surface preparations. For silver colloids and arrays of posts of definite shape and size the maximum enhancement were reported at a particular excitation frequency. In SERS, the Raman selection rules may be relaxed. Forbidden bands may arise in the SERS spectrum due to the relaxation in the symmetry of the molecule after a strong bond formation with the metal surface.

Second chapter deals with the theoretical interpretation (electromagnetic) of SERS. The origin of the enormous Raman enhancement is believed to come from the result of several mechanisms. There are two major types of mechanism that contribute to the effect : (i) electromagnetic and (ii) chemical. Electromagnetic interactions between the molecule and the substrate are believed to play a major role in the SERS process.

A metallic surface possesses surface plasmons. Raman enhancement results from excitation of these surface plasmons by the incident radiation. Enhancement also comes due to the excitation of surface plasmon by the Raman emission radiation. Other types of electromagnetic enhancement mechanisms are due to (i) concentration of electromagnetic field lines near high-curvature points on the surface, that is, the lightning-rod effect (ii) polarization of the surface by dipole-induced fields in adsorbed molecule, that is, the image field effect and (iii) Fresnel reflection effects. Chapter - II contains brief discussions on (i) electromagnetic sources of SERS effect (ii) surface plasmons (iii) electromagnetic enhancement on flat surfaces (image field model) and (iv) electromagnetic enhancement for spherical metal particles.

Chapter - III describes the chemical origin for the enhancement in the SERS process. There exists a 'chemical enhancement' for those molecules which are directly adsorbed on the metal surface. One promising model for a 'chemical effect' is a dynamical charge-transfer excitation of an electron from the metal to the adsorbate. Laser radiation of proper wavelength may excite a metal electron to the charge-transfer state causing the vibrational excitation of the molecule. When the electron is transferred back to the metal, the energy of the emitted photon is ultimately smaller than that of the incoming photon by one

vibrational quantum. Thus the Raman shift is determined by the molecular vibrations, even though the electron involved originates from the metal. According to this model, the large enhancement, is due to the fact that the scattering process is now resonant with the charge-transfer state.

Chapter - IV discusses the different techniques of SERS study. The production of suitable surface or media is essential for the observation of SERS. Few techniques those are described briefly in this chapter are (i) metal electrode (ii) colloidal metal particles (iii) metal island films (iv) silver-coated microsphere substrates (v) silver-coated fumed silica substrates (vi) silver-coated quartz posts (vii) metal-coated cellulose substrates (viii) silver membranes and (ix) chemically etched metal surfaces. The early experiments and much subsequent work on SERS have been done on silver electrodes randomly - roughened by electrochemical oxidation-reduction cycle in aqueous electrolytes. Strong SERS signals appear only after roughening the surface. The oxidation-reduction procedure generally produces surface protrusions in the size range of 25 - 500 mm on the electrode surface. The metal electrode technique of SERS is less favourable for probing the physics of enhancement, since it is difficult to measure some of their optical properties, particularly their absorption spectra, and to account for these properties, scientists paid their attention to more regular finely divided metal surfaces

viz. colloidal dispersions, evaporated island film or surface of a diffraction grating. The study of SERS on colloidal metal particles bears a significant role in proving the first clear demonstration that the enhancement in SERS is associated with the resonant excitation of electron density oscittations in metal surface. Colloidal solutions are prepared by reducing a dissolved metal salt by means of an appropriate reducing agent in either an aqueous or non-equeous medium.

Chapter - V contains brief description of (i) adsorption (ii) colloidal solution (iii) colour of a colloidal solution (iv) electrical charge of the colloidal particles (v) adsorption by colloids (vi) Ar^+ laser (vii) Ramanor U1000 doble monochromator etc. The process in which a layer of atoms or molecules of one substance forms on the surface of a solid or liquid, is called adsorption. The substance which adsorbs another substance, is called the adsorbent and the adsorbed substance is called adsorbate. Adsorption is a surface phenomenon. A colloidal solution is a state of matter intermediate between the true solution and a suspension. In a colloidal solution, the particles do not settle down and are not separable by ordinary filtration. Colloidal particles carry positive or negative charge and all particles of a given sol carry the some charge.

Chapter - VI have been devoted to the SERS study of 2-, 3- and 4-methylpyridines in silver colloidal solution. The

ordinary Raman and surface-enhanced Raman spectra of these molecules have been recorded in the spectral range of 150 - 1650 cm^{-1}. In case of 2-methylpyridine (2MP) it has been observed that the ring deformation modes are blue-shifted. It has also been found that the ring breathing mode is blue-shifted. These observations imply the formation of a bond between the Ag surface and the ring N-atom of the 2MP molecule. The formation of such bond limits the freedom of deformation of some of the modes and hence the shift towards the higher frequency. The absolute enhancement factors of different modes have been estimated, for 2MP, as 10^2 - 10^6. It has also been noticed that the in-plane ring vibrational modes have been enhanced more for 2MP and 3MP molecules. This implies the standing-up orientation of the 2MP and 3MP molecules on the surface of the sol particles. In the SERS spectrum of 3MP, a new band has been found at 320 cm^{-1} which is absent in the ordinary Raman spectrum. This band has been assigned to the Ag-N stretching mode. Appearance of this stretching mode confirms the formation of Ag-N bond. In 4-methylpyridince (4MP) molecule, it has been found that the ring breathing and bending modes are red-shifted. This implies the flat orientation of the 4MP molecule to the surface. For 4MP, it has been found that the out-of-plane vibrations have been enhanced more. This is also an additional evidence of forming 'flat-orientation' to the surface.

Chapter- VII discusses the normal Raman (NR) and SERS spectra of 2- and 3-chloropyridines in the range of 150 - 1650 cm^{-1}. The C - C bending modes for 2-chloropyridine (2CLP) at 180, 422 and 724 cm^{-1} have been shifted to 196, 436 and 736 cm^{-1} respectively in SERS. All these modes have been shifted towards the higher frequency. The ring breathing mode at 990 cm^{-1} has also been shifted to higher frequency at 1014 cm^{-1} in SERS. These observations support the formation of Ag-N bond between the silver surface and the ring N-atom of the 2CLP molecule. A new band appears at 284 cm^{-1} in SERS which has been assigned to be Ag-N stretching mode. It has also been found that the in-plane bending modes have been enhanced more. This implies the standing-up orientation of the molecule to the surface of the sol particle. Similar phenomena have been found for 3-chloropyridine (3CLP). Combination bands are observed in the SERS spectra of 2CLP and 3CLP.

Chapter - VIII has been devoted to the NRS and SERS study of 2-aminopyridine (2AP). The spectra were recorded in the range of 200 - 1650 cm^{-1}. The absolute enhancement factors have been estimated to be $\approx 10^3 - 10^6$ for different bands. The ring deformation modes ν_{16a}, ν_{6a}, ν_4 and ν_{12} are shifted towards the higher frequency. Ring breathing mode ν_1 has also been shifted to higher frequency. These findings are in favour of formation of a Ag-N bond. The observation of a new band in SERS at 330 cm^{-1} which has been assigned to Ag-N stretching mode,

confirms the formation of the Ag-N bond. It has been observed the in-plane modes have been enhanced more (even upto the order of $\approx 10^6$). This also implies the formation of Ag-N bond as well as the standing-up orientation of the adsorbed molecule. While recording the NRS of 2AP, background noise have been observed which does not appear in the SERS spectrum.

Chapter - IX treats the surface-enhanced Raman studies of 2- and 4-cyanopyridines. The spectra have been recorded in the spectral range of 400 - 2400 cm^{-1}. The C - C ring bending modes 430, 556, 590 and 782 cm^{-1} have been blue shifted to 444, 562, 612 and 788 cm^{-1} in the SERS. It has also been observed that the ring breathing mode ν_1 has been shifted from 1004 cm^{-1} to 1040 cm^{-1}. All these shift towards the higher frequency may be attributed to the formation of Ag-N bond as described earlier. The in-plane vibrational modes have been found more enhanced. This also helps us to conclude that the 2CP molecule takes-up the standing-up orientation. In the spectra of 4CP it has been found that the out-of-plane vibrations are enhancing more. It has been observed that the ring breathing mode has been shifted to lower frequency (from 1008 cm^{-1} to 998 cm^{-1}). All the C - C out-of-plane bending modes (species a_2 or b_1) have been red-shifted in SERS. These observations imply the flat-orientation of the 4CP molecule on the surface of the silver colloidal particles.

Finally, we can make a propensity rule on the basis of the present investigations of SERS of pyridine derivatives. The derivatives having their substituents at the 2- or 3-positions are being adsorbed in the 'standing-up' orientation whereas the derivatives having the substituents at 4-position are getting adsorbed on 'flat' orientation. The in-plane bending modes are enhancing more for standing-up orientation and out-of-plane banding modes are getting more enhanced for 'flat' orientation. Ring breathing and C - C bending modes are shifting towards the higher frequency for standing-up orientation and towards the lower frequency for flat orientation of the adsorbed molecules.

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DEDICATED TO
MY PARENTS
WIFE
CHILDREN

DR. Y. KUMAR
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CERTIFICATE

Certified that the work presented in the thesis entitled **"Surface Enhanced Raman Scattering (SERS) Studies of Some Pyridine Derivatives"** is the original work of **Mr. Mohd. Ekram Ali Shaikh** carried out under my supervision.

(DR. Y. KUMAR)

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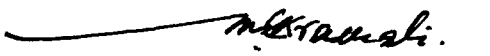

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1. **E.A. Shaikh** and Y. Kumar; Applications of surface-enhanced Raman scattering (SERS) for biomolecules; Indian Journal of Physics, **65B** (6) 655 (1991).

2. **E.A. Shaikh** and Y. Kumar; Surface-enhanced Raman scattering (SERS) of pyridine adsorved on silver colloidal particles; II IPA/DST Symp. on Laser and Applications, Banaras Hindu University, Varanasi, Dec. 11 - 15, 1989.

3. **E.A. Shaikh** and Y. Kumar; Applications of surface-enhanced Raman scattering for biomolecules; National Symposium on Biophysics; Saha Institute of Nuclear Physics; Calcutta. Feb. 20 - 22, 1990.

4. **E.A. Shaikh** and Y. Kumar; **Surface Enhanced Raman** Scattering (SERS) of pyridine adsorbed on silver sol; National Symposium on Chemical Physics, Pondicherry University, Pondicherry. Feb. 9 - 11, 1990.

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9. **E.A. Shaikh,** Y. Kumar and B.N. Khanna; Surface Enhanced Raman Scattering (SERS) Investigations of 2-, 3- and 4-methylpyridines Adsorbed on Silver Sol. Sent for Publication .

10. **E.A. Shaikh,** Y. Kumar and B.N. Khanna; Surface Enhanced Raman Scatterings (SERS) Studies of 2- and 3-chloropyridine Adsorbed on Silver Hydrosol. Sent for Publication.

11. **E.A. Shaikh,** Y. Kumar and B.N. Khanna; Surface Enhanced Raman Scattering (SERS) of Some Pyridine Derivatives; XV International Conf. on Raman Spectrocopy, to be communicated.

CONTENTS

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INTRODUCTION

1.1 GENERAL

1.2 DISCOVERY OF SERS

1.3 NATURE OF SERS

1.4 SCOPE OF SERS

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1.1 General

When an intense beam of monochromatic light is allowed to pass through a substance in the solid, liquid or gaseous state, the molecules of the substance will scatter the light. The scattered light contains some additional frequencies above and below that of the incident frequency. This phenomenon is known as the Raman scattering which provides valuable information about the structure and properties of the molecules being irradiated. The difference between the frequency of the incident light and that of the Raman lines is called the Raman shift. This Raman shift corresponds to the vibrational (also rotational and electronic in particular cases) frequencies present in the molecules of the sample.

The Raman process itself—inelastic light scattering by molecular vibrations - is inherently weak. Only a small fraction, 10^{-6} or so, of the photons incident on a sample are Raman scattered. Thus a major limitation of the conventional Raman method is its low sensitivity. Recently, the Raman technique has enjoyed an increased interest among the spectroscopists following the observation of enormous Raman enhancement for some molecules adsorbed on special metal surfaces. There are certain molecules which when adsorbed on specially prepared metal surfaces or on metal colloids exhibit inordinate Raman signals whose intensity is $\approx 10^2 - 10^6$ times larger than the normal Raman signals. This enormous increase

in Raman signal arises from a surface enhancement process and the phenomenon has been christened as Surface Enhanced Raman Scattering (SERS).

1.2. Discovery of SERS

In 1974, Fleischmann et al [1] reported strongly enhanced Raman scattering from pyridine molecules adsorbed from aqueous solution onto silver electrode surface that had been roughened electrochemically by successive oxidation-reduction cycles. They apparently believed that the inordinate signal strength is coming due to a large increase in the electrodes' surface area. In 1977, Jeanmair et al [2] and independently Albrecht et al [3] first recognized that the large intensity could not be accounted for by the increase in surface area alone. They showed that the increase in SERS signals obtained by roughening the electrode surface area too slightly is equal to that obtained by extending the electrodes' surface area ten times.

Almost all early studies on SERS were performed with pyridine on roughened silver electrodes. Since then the effect has been reported for a few hundred molecules adsorbed on Ag, Au, Cu, Li, Na, K, In, Al, pl and Rh. Silver is the most studied and the most efficient SERS metal, although the alkalis seems to produce SERS signals rivaling that of silver.

1.3 Nature of SERS

Surface-enhanced Raman scattering (SERS) was first detected in pyridine, C_5NH_5, adsorbed at sliver electrodes. If one starts with a smooth silver electrode, e.g. a silver deposited at room temperature, a strong Raman signal from the vibrational lines of pyridine appears only after an electrochemical oxidation-reduction cycle. After analyzing the results of all experiments on SERS, it has been widely accepted that the surface roughness is a pre-requisite for SER effect. When appropriately roughened, a silver surface can induce a SERS enhancement factor of 10^6, whereas a mirror like smooth silver surface produces only 400-fold Raman enhancement [4]. The dependence of the SERS enhancement on surface roughness exhibits different excitation profiles for different surface preparations. For silver colloids and arrays of posts of definite shape and size the maximum enhancement was reported at a particular excitation frequency.

The SERS phenomenon has excitation characteristics that are similar to those observed with Normal Raman Scattering (NRS). The intensity of the scattered light is dependent on that of the incident light. The scattered light is depolarized even with molecules such as pyridine, which exhibits highly polarized NRS.

The SERS effect appears to occur under specific experimental conditions based on (a) special requirments on the

dielectric constant and (b) the morphology of the surface under study. Selection criteria of the type of substrates and media that are SERS active are based on several considerations. The type of the metal on the surfaces is an important factor. The SERS phenomenon occurs mostly on specific metallic surfaces. Silver exhibits the strongest enhancement effects followed by copper and gold.

In SERS, the Raman selection rules are relaxed, as detected for pyrazine on silver by Dornhaus et al [7] and Erdheim et al [8] and for benzene on silver by Moskovits and DiLella [9]. Normally forbidden bands arise in the spectrum of an adsorbed molecule due to the reduction in the symmetry of the molecule after a strong bond formation with the surface [10]. The appearance of Raman forbidden lines may also come due to the steep electric field gradient that exists near an illuminated metal surface.

1.4 Scope of SERS

The discovery of the SER effect has stimulated an immense interest in fundamental research. Raman spectroscopy as a probe of surface structure and dynamics has developed its potential due to SERS. Besides producing much affinity in Raman spectroscopy of surfaces, the discovery of SERS has animated and resurrected the activity in classical electrostatic and

electromagnetic theory, especially as applied to small particles; in the problem of radiating multipoles near metal surfaces, in the optical properties of small particles and in the generation of surface plasmons. It has encouraged the experiments like second-harmonic generation from molecules at surfaces by bringing the general area of surface-photon interactions to the foreground. Theoretical and experimental investigations of the properties of metallic gratings and molecules placed near them has greatly increased due to the continuous interest in SERS. The discovery of SERS has also renewed interest in the properties of aqueous metal sols, a well-established field of science that had fallen on hard times. This renaissance coincided to some extent with a growing interest in non-metal colloids such as those of polymers.

One important new direction in experimental SERS has been the successful union of the Langmuir-Blodgett technique and surface-enhanced spectroscopy. There was a great need in the field of Langmuir-Blodgett (LB) mololayers for a sensitive method for characterization of monolayers and interfaces consisting of LB films. SERS has emerged as a powerful technique for spectroscopic characterization of LB layers [11].

An interesting application of SERS has been recently developed in the field of photographic sciences. Since SERS allows structurally sensitive investigations of adsorbed molecules in very low concentrations, SERS spectra of sensitizing dyes can

be recorded which give information about the chemical structure of these molecules as well as their adsorption behaviour, aggregation and formation of radicals. Moreover, the SERS enhancement factor shows correlations to photographically important properties of silver halide emulsion and of the sensitizing dyes [12, 13].

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C H A P T E R - II

THEORETICAL INTERPRETATION OF SERS - I
[Electromagnetic Effect]

2.1 GENERAL

2.2 ELECTROMAGNETIC SOURCES OF SERS EFFECT

2.3 SURFACE PLASMONS

2.4 ELECTROMAGNETIC ENHANCEMENT ON FLAT SURFACES : Image Field Model

2.5 ELECTROMAGNETIC ENHANCEMENT FOR SPHERICAL METAL PARTICLES

REFERENCES

2.1 General

Extensive research efforts have been devoted to the determination and understanding of the sources of surface-enhanced Raman scattering (SERS) effect. There is no single theoretical model capable of accounting for all the experimental observations related to SERS. The origin of the enormous Raman enhancement is believed to come from the result of several mechanisms. There are two major types of mechanism that contribute to the effect : (i) electromagnetic and (ii) chemical.

2.2 Electromagnetic Sources of SERS Effect

Electromagnetic interactions between the molecule and the substrate are believed to play a major role in the SERS process. During the interaction a large local electromagnetic field is created which enhances the Raman signals. A major contribution to electromagnetic enhancement is due to the surface plasmons. Surface plasmons are associated with the collective excitations of surface conduction electrons in metal [1]. Raman enhancements result from excitation of these surface plasmons by the incident radiation. Another enhancement is due to the excitation of surface plasmons by the Raman emission radiation of the molecule. Other types of electromagnetic enhancement mechanisms are due to (i) concentration of electromagnetic field lines near high-curvature points on the surface, that is, the

lightning-rod effect [2,3] (ii) polarization of the surface by dipole-induced fields in adsorbed molecules, that is, the image field effect [3,4,5] and (iii) Fresnel reflection effects.

2.3 Surface Plasmons

A plasma is an electrically neutral collection of electron and positive ions. A plasma can undergo oscillations due to an external source of excitation. A plasmon is nothing but a quantum of the plasma oscillations that occur in a plasma. At the surface between a plasma and material of dielectric constant ϵ_o a surface plasmon exists whose energy is given by

$$E_s = \hbar \omega_p / (1 + \epsilon_o)^{\frac{1}{2}} \qquad (2.1)$$

which is confined to within a screening length of the surface. Surface plasmons are the quanta of surface plasma oscillations, sometimes called surface electromagnetic waves, propagate parallel to the surface. For a free electron metal the surface plasma frequency ω_s is given by

$$\omega_s = \omega_p / (1 + \epsilon_o)^{\frac{1}{2}} \qquad (2.2)$$

where ω_p is the bulk plasma frequency [6]. When the metal is in contact with a vacuum,

$$\omega_s = \omega_p / 2^{\frac{1}{2}} \qquad (2.3)$$

The surface plasmon has the parallel momentum $K_{\parallel}$ which is given by the relation,

$$K_{\parallel}^{\,2} = \left(\frac{\omega}{c}\right)^2 \mathrm{Re}\,\frac{\epsilon_o \epsilon}{\epsilon_o + \epsilon} \qquad (2.4)$$

where, ϵ is the complex dielectric function of the metal (or conductor) and ϵ_o is that of the ambient. Due to the requirement of the momentum conservation, surface plasmons cannot be excited optically, hence a surface plasmon does not radiate but is confined to the metal surface. Surface plasmon excitation becomes possible if the parallel momentum of the incident photon is modified to match that of the plasmon. This can be done by using a prism with carefully chosen refractive index or by constructing a grating on the surface to change the photon parallel momentum by diffraction. Making a surface randomly rough is also equivalent to ruling the grating on it. So, the surface plasmon can radiate under this condition.

Small particles have electromagnetic resonances similar to the surface plasmon. When the particle is small compared to the wavelength of the incident plane wave, a plasmon can be excited that has the symmetry of a time-varying dipole. Once excited, this dipolar plasmon can, of course, radiate. For a sphere this resonance occurs at the frequency ω_R, for which the following condition is to be satisfied,

$$\mathrm{Re}\,[\ \epsilon(\omega_R)\ ] = -2\,\epsilon_o \qquad (2.5)$$

A sphere has also other resonances whose frequencies may be obtained from the relation,

$$\mathrm{Re}\left[\ \epsilon(\omega_N)\ \right] = -\left[\ \frac{N+1}{N}\ \right]\epsilon_o \qquad (2.6)$$

where N is an integer. Except for N = 1 resonance, which is dipolar, the others have symmetries corresponding to higher multipoles and therefore cannot radiate.

2.4 Electromagnetic Enhancement on Flat Surfaces : Image Field Model

Electromagnetic interaction between a molecule and a flat surface plays a vital role in the enhancement of the Raman signals. King and his collaborators [7] calculated this enhancement by the help of a model which is known as "image-field model". According to this model, the dipole moment induced in the molecule by the incident field and its image field is given by,

$$\mu = \alpha\,(E + E_{im}) \qquad (2.7)$$

where E and E_{im} are the incident and image fields, and α is the ZZ component of the molecular polarizability. E_{im} is given by

$$E_{im} = \frac{\epsilon - \epsilon_o}{\epsilon + \epsilon_o} \cdot \frac{\mu}{4r^3} \qquad (2.8)$$

where r is the distance between the point dipole and the surface.

Substituting and rearranging we can get,

$$\mu = \frac{\alpha}{1-(\alpha/4r^3)(\epsilon-\epsilon_o)/(\epsilon+\epsilon_o)} \cdot E \qquad (2.9).$$

This expression resembles to a conventional expression for a dipole moment μ induced by a field E except that in place of the polarizability α one has an effective polarizability,

$$\alpha_{eff} = \frac{\alpha}{1-(\alpha/4r^3)(\epsilon-\epsilon_o)/(\epsilon+\epsilon_o)} \qquad (2.10).$$

This expression has a pole at the frequency at which

$$\mathrm{Re}\left[\frac{\alpha(\epsilon-\epsilon_o)}{4r^3(\epsilon+\epsilon_o)}\right] = 1 \qquad (2.11).$$

In fact this is related to surface-plasmon excitation in the metal surface at the frequency for which the condition $\mathrm{Re}(\epsilon) = -\epsilon_o$ obtains [8]; otherwise, the quantity, $\alpha(\epsilon-\epsilon_o)/4r^3(\epsilon+\epsilon_o)$ would not approach 1 except for unrealistically small values of r. Using reasonable parameters, King et al [7] showed that on silver, Raman enhancements in excess of 10^6 are possible at or below r = 1.65 Å, the enhancement dropping to around 10^2 for r = 2 Å.

Feibelman [9] finds practically no image-field enhancement in a model that uses linear response theory to treat the response of the metal electrons to the time-varying induced dipole due to the adsorbed molecule. Lee and Birman [10,11] have considered the image-field problem as part of their general

coupled-state quantum formalism for treating SERS. So, according to them the image-field enhancement is not an important contributor to SERS.

A decidedly real surface-enhancement process, electromagnetic in origin, which occurs at flat metal surfaces is due to the fact that the molecule near the metal surface is illuminated by both a direct and a reflected field, coherently superimposed to give an intensity upto four times the incident intensity. Likewise, the Raman scattered field is composed of a direct and reflected field yielding upto four-fold an increase in its intensity for a total maximum enhancement of 16. Efrima and Metiu [12,13,14] has called this effect as 'minor' enhancement.

2.5 Electromagnetic Enhancement for Spherical Metal Particles

Let us consider a metallic spherical particle. A molecule, treated as a classical electric dipole, is placed at a position r', outside the particle. Upon irradiation with a plane wave of frequency ω_o, the molecular dipole will radiate at the Raman frequency ω with a dipole moment

$$\vec{P}(\vec{r}', \omega) = \alpha' \vec{E}_p(\vec{r}', \omega_o) \qquad (2.12)$$

where α' is the Raman polarizability of the molecule and $\vec{E}_p(\vec{r}', \omega_o)$ is the field at the exciting frequency ω_o at the location of the molecule [15].

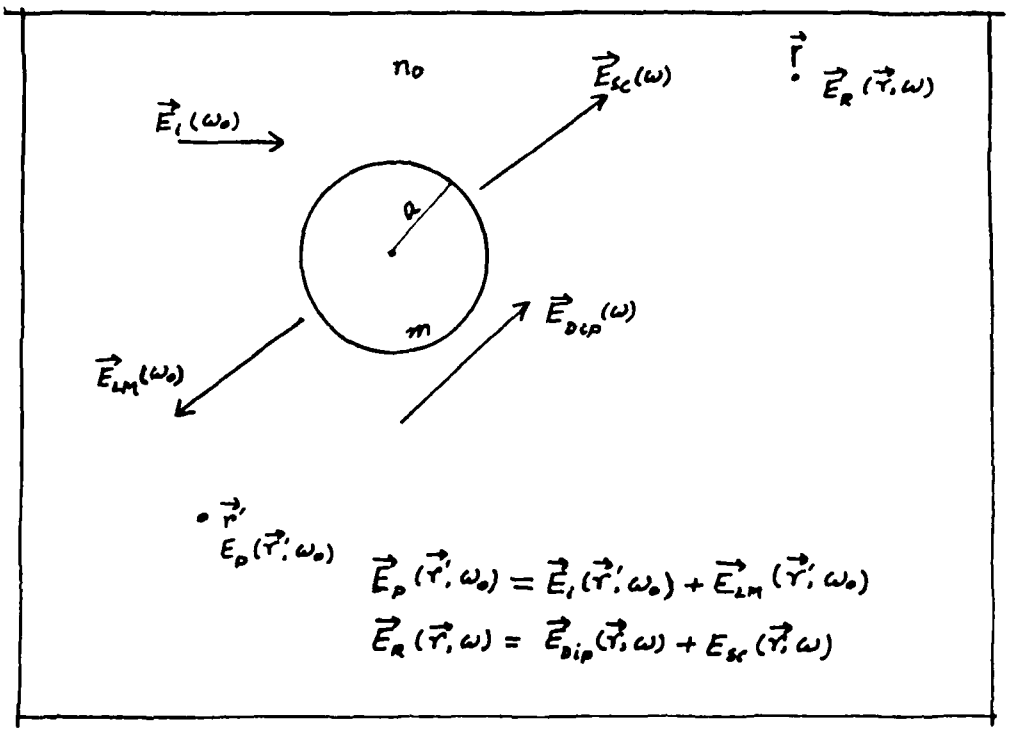

Fig. 2.1 : Schematic view of electric fields near a sphere of radius 'a' and refractive index 'm'. At the incident frequency ω_0 there are the incident, Lorentz-Mie, and primary fields, $E_i(\omega_0)$, $E_{LM}(\omega_0)$ and $E_p(r', \omega_0)$. At the shifted frequency ω there are the dipole, scattered, and Raman fields, $E_{DIP}(\omega)$, $E_{sc}(\omega)$ and $E_R(r, \omega)$, where r' and r are the positions of the dipole and observer respectively.

The exciting field in turn is comprised of the incident field $\vec{E}_i(\vec{r}', \omega_o)$ plus the elastically scattered field $\vec{E}_{LM}(\vec{r}', \omega_o)$ called the Lorentz-Mie field. Hence,

$$\vec{E}_p(\vec{r}', \omega_o) = \vec{E}_i(\vec{r}', \omega_o) + \vec{E}_{LM}(\vec{r}', \omega_o) \qquad (2.13).$$

The electric field associated with the Raman radiation at an observation point $\vec{r}$ is given by

$$\vec{E}_R(\vec{r}, \omega) = \vec{E}_{dip}(\vec{r}, \omega) + \vec{E}_{sc}(\vec{r}, \omega) \qquad (2.14)$$

where $\vec{E}_{dip}$ is the field of the oscillatcry dipole $\vec{P}(\vec{r}', \omega)$ in the absence of the particle and $\vec{E}_{sc}(\vec{r}, \omega)$ is a secondary or scattered field that must be computed by solving the appropriate boundary value problem at the Raman frequency

Again let us consider that the radius of the particle is 'a' and ϵ_1 and ϵ_2 are the complex dielectric function of the particle i.e. metal and of the surrounding medium. In the small-particle limit, the electric field at ω_o and r' may be considered equivalent to the field of an electric dipole at the center of the sphere with dipole moment

$$\vec{P}_o = a^3 g_o \vec{E}_i(\vec{r}', \omega_o) \qquad (2.15)$$

where, $$g_o = \frac{\frac{\epsilon_1(\omega_o)}{\epsilon_2(\omega_o)} - 1}{\frac{\epsilon_1(\omega_o)}{\epsilon_2(\omega_o)} + 2} = \frac{\epsilon - 1}{\epsilon + 2} \qquad (2.16)$$

in which ϵ is the ratio of the complex dielectric function of the material comprising the particle to that of the ambient.

$\vec{E}_p$ will force the molecule at $\vec{r}'$ to oscillate at the shifted frequency ω with dipole moment

$$\vec{P}_i(\omega) = \alpha \vec{E}_p(\vec{r}', \omega_o) \tag{2.17}$$

where α is the Raman tensor of the free molecule and $\vec{E}_p(\vec{r}', \omega_o)$ is the incident field plus the Lorentz-mie field, which is now due to the dipole $\vec{P}_o$.

Again, the scattered field $\vec{E}_{sc}(\vec{r}, \omega)$ is the field of an electric dipole which is located at the center of the particle with a dipole moment,

$$\vec{P}_2(\omega) = a^3 g \vec{E}_d(0, \omega)$$

where,
$$g = \frac{\frac{\epsilon_1(\omega)}{\epsilon_2(\omega)} - 1}{\frac{\epsilon_1(\omega)}{\epsilon_2(\omega)} + 2} = \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} \tag{2.18}$$

in which $\vec{E}_d$ is the field of $\vec{P}_2(\omega)$ at the origin $\vec{r}' = 0$ in the absence of the sphere. The total Raman emission is given by the coherent addition of the field of $\vec{P}_1(\omega)$ and $\vec{P}_2(\omega)$.

In the most favourable configuration when the molecule is on the surface of the sphere ($r' = a$) and the polarization of the incident and scattered wave is perpendicular to the scattering

plane, the Raman enhancement factor G for the adsorbed molecule is given by Kerker et al [16] as

$$G = 5\left|(1 + 2g_o) (1 + 2g)\right|^2 \qquad (2.19).$$

When a sphere is entirely covered with adsorbed molecules, one must extend this analysis by averaging the Raman scattered light emanating from every molecule. Kerker et al [16] and Wang et al [17] have performed this averaging with the assumption that each admolecule to be an oscillating dipole normel to the surface. This yields the result,

$$G = \left|(1 + 2g) (1 + 2g_o)\right|^2 \qquad (2.20)$$

independent of the choice of polarization direction of the incident or scattered light.

Now, let us focus to the eqn. (2.19) which is the expression for the enhancement when a single molecule is adsorbed on the sphere. Here, the quantity g (or g_o) becomes large when Re (ϵ) approaches - 2. This is precisely the condition for the excitation of localized surface plasmons in the sphere. When that condition obtains, eqn. (2.19) is dominated by the $g.g_o$ term and G becomes

$$G = 80\left|g.g_o\right|^2 \qquad (2.21).$$

Hence according to this model, large SERS signals are expected when both the frequency of the incident and Raman scattered beams approaches the surface-plasmon resonance conditions. In this case the quantity G becomes proportional to $[\ (\epsilon'-1)/\epsilon''\ ]^4$ i.e.

$$G \propto \frac{\epsilon'-1}{\epsilon''} \tag{2.22}$$

where ϵ' and ϵ'' are respectively, Re (ϵ) and Im (ϵ). Hence the metals which provide the greatest enhancement, according to this model, are those that have small ϵ'' values and large ϵ' values at the frequency at which Re (ϵ) = -2. This condition immediately brands the alkali metals (gr. Ia) and the coinage metal (gr. Ib) as good enhancers, producing G values in excess of 10^5.

Lastly, the size of the particle is an important factor for observing the enhancement. In the electromagnetic theory of SERS observed from molecules adsorbed on spherical metal particles, a strong enhancement will be observed when the particle size remains smaller than the exciting wavelength. It should be mentioned that for larger spherical particles, the enhancement factor decreases due to (i) radiation damping and (ii) dynamic depolarization i.e. the partially destructive interference between radiation emitted at different points of the particle.

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C H A P T E R - III

THEORETICAL INTERPRETATION OF SERS - II
[Chemical Effect]

3.1 General

Surface-enhanced Raman scattering has been observed only on rough metal surfaces. This is at least in part, a consequence of an enhancement of the electric field at the surface due to excitation of plasmon-type resonance. Depending on the model for the rough surface, enhancements of the order $10\text{-}10^4$ can be explained by this means. There are evidences, however, that the enhancement of the field alone cannot account for the whole effect. For example, since the electromagnetic model rely on enhancement in the electromagnetic field without any change in molecular properties, the enhancement should be equal irrespective of the kind of molecule concerned. But it has been observed that SERS is different for different molecules. Again, it has been found experimentally that when several monolayers of pyridine are successively adsorbed on a Ag metal surface, the molecules in the first monolayer have a Raman cross section about 100 times larger than molecules in the following monolayers [1,2]. These examples show that the electromagnetic mechanism cannot fully explain all the experimental results and thus there exists an additional 'chemical enhancement' for those molecules which are directly adsorbed on the metal surface [3].

One promising model for a "chemical effect" is a dynamical charge transfer excitation of an electron from the metal to the adsorbate giving rise to a resonance effect in the Raman cross section of the adsorbate. According to Persson [4], the

charge-transfer excitations between the metal and the adsorbed molecules can give rise to an enhancement of $\approx 10^2$. Chemical enhancements of the same order of magnitude have been calculated by Kirtley et al [5] and McCall et al [6]. On the other hand Yamada [7] has estimated the charge-transfer contribution as $\approx 10^3$.

3.2 Charge-Transfer (CT) Contribution to SERS

Interaction of electron donors and acceptors leads to formation of charge transfer complexes. In the ground state the partners (i.e. the adsorbate and adsorbent) are weakly bound and the wave function resembles more or less that of independent components, with a small admixture of an ionic structure where an electron is transfered from one partner to the other one. In the excited state, however, the ionic structure dominates strongly and bonding in the complex is much more pronounced. Recently it has been observed by electron-energy loss spectroscopy (EELS) that the various molecules which exhibit SERS, after adsorption to silver, show a new electronic transition not present either in the isolated molecule nor in the metal [8,9]. These transitions have been ascertained as the charge transfer transitions of metal electrons from below the Fermi energy to an unoccupied state of the molecule. Some authors [4,10,11] have developed a charge transfer model for SERS on the basis of above-finding. In this model, laser radiation of proper wavelength may excite a metal

electron to the charge transfer state causing the vibrational excitation of the molecule. When the electron is transferred back to the metal, the energy of the emitted photon is ultimately smaller than that of the incoming photon by one vibrational quantum. Thus the Raman shift is determined by the molecular vibrations, even though the electron involved originates from the metal. According to this model, the large enhancement, is due to the fact that the scattering process is now resonant with the charge-transfer state. Persson's [4] model of CT effect is emerging in which he considered the Newns-Anderson resonances of an adsorbate of a silver surface and the model has been described below in short.

Let us describe the electronic structure of atoms and small molecules by denoting the orbitals as $|i\rangle$ and energy levels ϵ_j. Let the density of states be given by,

$$\rho(\epsilon) = \sum_i \delta(\epsilon - \epsilon_i) \tag{3.1}$$

or the density of states projected on an orbital $|a\rangle$:

$$\rho_a(\epsilon) = \sum_i |\langle a|i\rangle|^2 \delta(\epsilon - \epsilon_i) \tag{3.2}.$$

Fig. 3.1 shows the density of states $\rho(\epsilon)$ of bulk silver. The energy scale is chosen in such a way that $\epsilon = 0$ at the Fermi energy. The shaded area of Figs. 3.1 and 3.2 corresponds to occupied levels ($\epsilon < 0$). The main contribution to $\rho(\epsilon)$ for $-7 < \epsilon < -3$eV originates from the 4d levels of the Ag atoms while

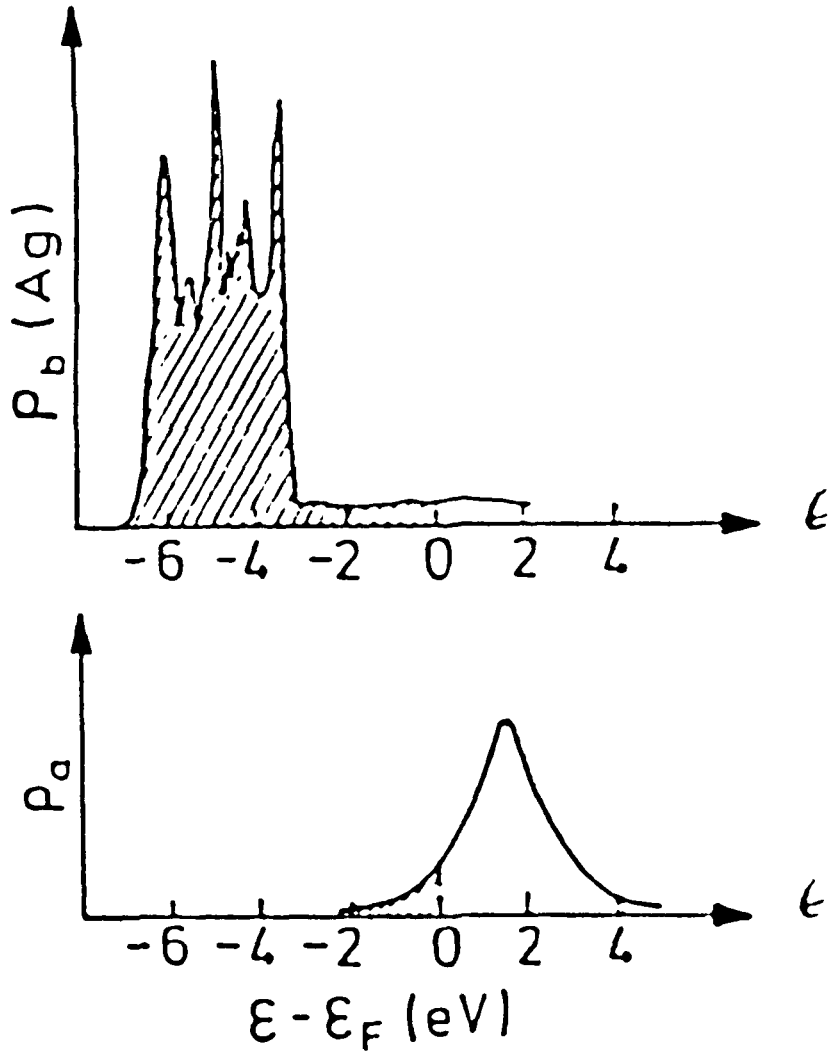

Fig. 3.1 : Induced density of states ρ_a associated with all imagined molecule adsorbed on a metal surface, ϵ is measured in ev relative to the Fermi energy.

for $\epsilon > -3$eV mainly consists of the 5sp levels.

Let us consider a molecule with an orbital $|a\rangle$. As the molecule comes near the metal the originally sharp level may broaden by interaction with the metal, i.e. by the fact that tunneling of electrons between the orbital $|a\rangle$ and the metal gives it a finite life-time and hence a halfwidth 2Γ. That is, the density of states projected on the orbital $|a\rangle$, which in the free molecule is a Dirac delta function,

$$\rho_a^{free}(\epsilon) = \delta(\epsilon - \epsilon_a) \tag{3.3}$$

becomes broadened :

$$\rho_a^{adsorbed}(\epsilon) = \pi^{-1} \frac{\Gamma(\epsilon)}{[(\epsilon - \tilde{\epsilon}_a(\epsilon)]^2 + \Gamma^2(\epsilon)} \tag{3.4}.$$

It should be noticed that the original level is not only broadened but is also shifted in energy.

Persson assumed that the adsorbed molecule has a broadened level, $\rho_a(\epsilon)$, located in the vicinity of the Fermi energy and therefore only partly filled (Fig. 3.2). The occurrence of a partially filled adsorbate-induced resonance is a very common phenomenon in chemisorption [12]. So, for example, whenever there is a non-integer charge transfer between the adsorbed molecule and the metal, there must be at least one partially filled resonance.

Persson calculated the ratio of Raman scattering intensity of the adsorbed molecule with respect to the free molecule. The photon-electron interaction is simply given by

$$H_{\text{photon-electron}} = - e.d.\, E_z .\, \hat{n}_a \qquad (3.5)$$

where d is the distance of the "center of charge" of the orbital $|a\rangle$ to the metal image plane, E_z the incident field normal to the surface, and $\hat{n}_a$ the operator describing the number of electrons in orbital $|a\rangle$.

The electron-molecule vibration interaction is given by

$$H_{\text{electron-vibr}} = \epsilon'_a(0).\, Q\, \hat{n}_a \qquad (3.6)$$

where $\epsilon'_a(0)$ stems from the expansion of the energy ϵ_a of the orbital $|a\rangle$ of the free molecule with respect to the normal coordinate Q of the vibration,

$$(Q) = \tilde{\epsilon}_a + \epsilon'_a(0))\, Q + \ldots\ldots \qquad (3.7).$$

It should be noted that for Q = 0, the energy of the neutral molecule, not of the "negative ion state", is at a minimum. The "chemical enhancement" ratio η_{chem} thus becomes :

$$\eta_{chem} = |(ed)^2.\ \epsilon'_a(0).\, G\,(\,\omega_L, \omega\,)/\alpha'(0)/2|^2 \qquad (3.8)$$

$\alpha'(0)$ is the derivative of the electronic polarizability of the free molecule with respect to Q which governs the ordinary non-resonant Raman scattering, ω_L is the laser frequency, ω the

Stoke's frequency and $G(\omega_L, \omega)$ contains the resonant Raman scattering caused by the charge-transfer excitation.

3.3 Summary of SERS Theories

It is by now generally believed that one or more of the following effects, together with the surface roughness, play an important role in SERS process.

(i) The bounded metal has plasmon modes which are localized near the surface and have large field amplitudes there. If an incident or scattered photon can excite these modes substantially, the molecule will be exposed to large effective fields varying with the frequency of the incident or scattered photon. As a result, the electron-photon (e - p) interaction and hence the cross section will be enhanced.

(ii) The incident or scattered photon fields can be substantially changed due to polarization effects associated with the presence of the molecule. For instance, all kinds of real or virtual dipolar tansitions on the molecule induce image dipoles in the metal and thus change the electric field.

(iii) The electronic levels of the molecule may shift or broaden because of chemisorption effects. Thus the initial, final and intermediate electronic states for the scattering process may change compared with the free molecule.

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C H A P T E R - IV

DIFFERENT TECHNIQUES OF SERS

4.1 General

SERS process is an interesting one but the main drawback of the system for analytical applications is the production of suitable surface or media that have an easily controlled protrusion size and reproducible structures. Some techniques of the SERS study which have been reported are :

(i) Metal electrodes

(ii) Colloidal metal particles

(iii) Metal island films

(iv) Silver-coated microsphere substrates

(v) Silver-coated fumed silica substrates

(vi) Silver-coated Quartz posts

(vii) Metal-coated cellulose substrates

(viii) Silver membranes

(ix) Chemically etched metal surfaces

4.2 Metal Electrodes

SERS was first observed by Fleischmann and Hendra in pyridine molecules adsorbed on silver electrode [1]. Afterwards, so many investigations have been carried out on other metal electrodes [2 - 5]. The intensity of Raman scattering is strongly dependent on the state of roughness of the metal surface. The early experiments and much subsequent work on SERS have been done on silver electrodes randomly-roughened by an electrochemical oxidation-reduction cycle in aqueous electrolysis.

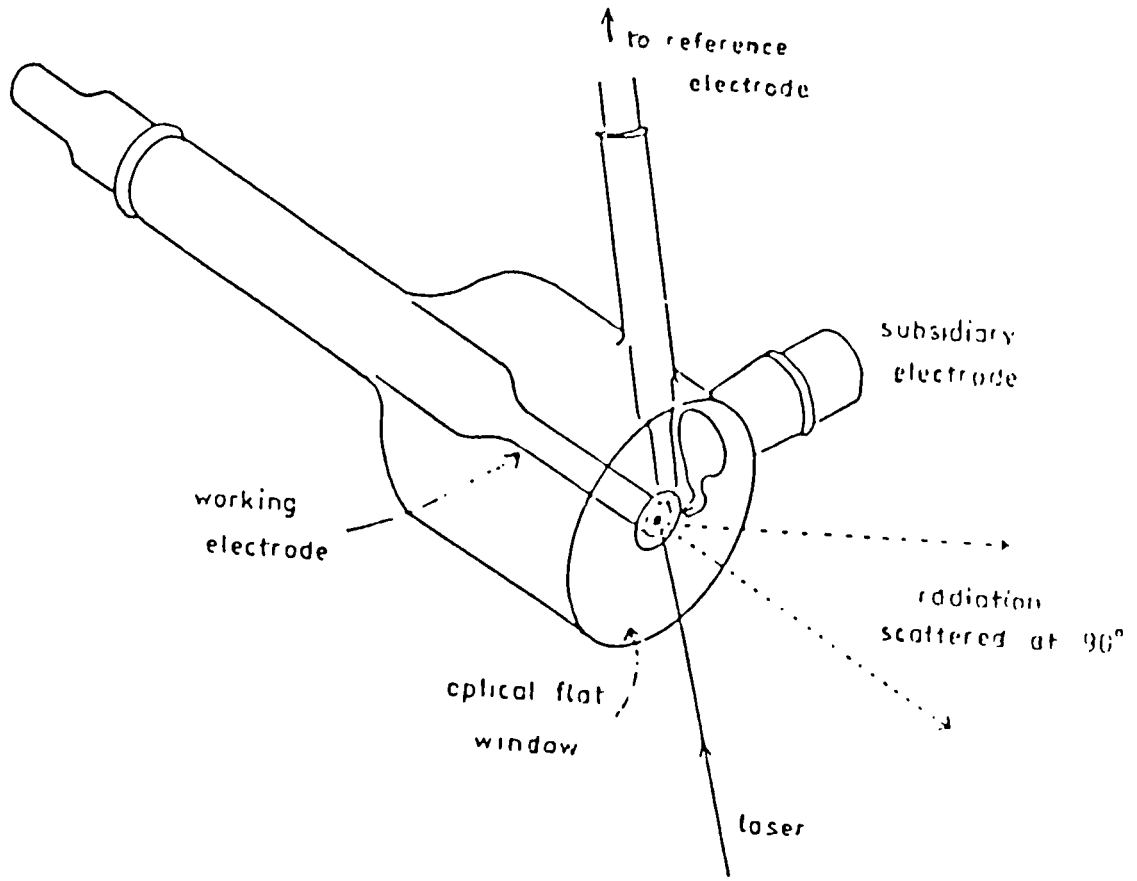

Fig. 4.1 : Electrochemical Cell

Fig. 4.1 shows a diagram of the electrochemical cell originally used by Fleischmann and Hendra [1]. A polycrystalline silver rod is illuminated on its end face at an angle of incidence of about 60° by a focussed laser beam, which enters through the flat end window of the glass cell. The area of the surface illuminated by the focussed laser is imaged through the end window onto the spectrometer entrance slit with the usual large aperture collection lens arrangement so as to collect the Raman scattered light, which is emitted in a relatively narrow cone [6,7]. The cell is filled with electrolyte containing the adsorbate, and the silver rod is sleeved in teflon so that only the end face is exposed to electrochemical action. The cell carries secondary and reference electrodes for potentiostatic or other electrochemical control of the metal electrolyte interface. The working electrode is generally placed in a position such that the laser excitation can be focused onto its surface, and the Raman scattered light can be efficiently collected by appropriate optics. Strong SERS signals appear only after electrochemical oxidation— reduction cycles performed on the metal electrode. During the first half of a cycle, silver at the electrode is oxidized by the reaction,

$$Ag \longrightarrow Ag^{+} + e^{-}.$$

During the reduction half cycle, a roughened silver surface is produced by the reaction,

$$Ag^{+} + e^{-} \longrightarrow Ag.$$

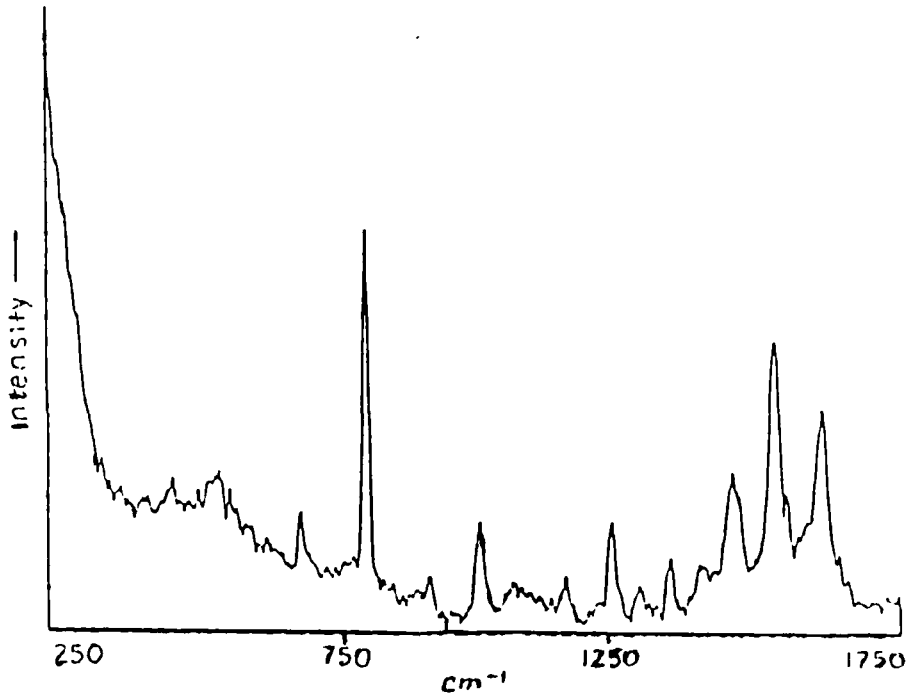

Fig. 4.2 : SERS spectrum of dimethylcytosine adsorbed on copper colloids (Repoduced from ref. 9)

This oxidation-reduction procedure generally produces surface protrusions in the size range of 25 - 500 nm on the electrode surface.

4.3 Colloidal Metal Particles

The metal electrode technique of SERS is less favourable for probing the physics of enhancement, since it is difficult to measure some of their other optical properties, particularly their absorption spectra, and to account for these properties, scientists drew their attention to more regular finely divided metal surfaces, viz. colloidal dispersions or evaporated island film, or the surface of a diffraction grating. The study of SERS on colloidal metal particles bears a significant role in proving the first clear demonstration that the enhancement in SERS is associated with the resonant excitation of electron density oscillations in metal surface.

Colloidal solution is prepared by reducing a dissolved metal salt by means of an appropriate reducing agent in either an aqueous or non-aqueous medium. Surface-enhanced Raman scattering by colloidal metal particles was first reported by Creighton et al [8], who made investigation of SERS on pyridine adsorbed on aqueous silver and gold colloids. Silver colloids are generally prepared by rapidly mixing a 1.0×10^{-3}M aqueous solution of $AgNO_3$ with 2.0×10^{-3}M aqueous solution of ice-cold

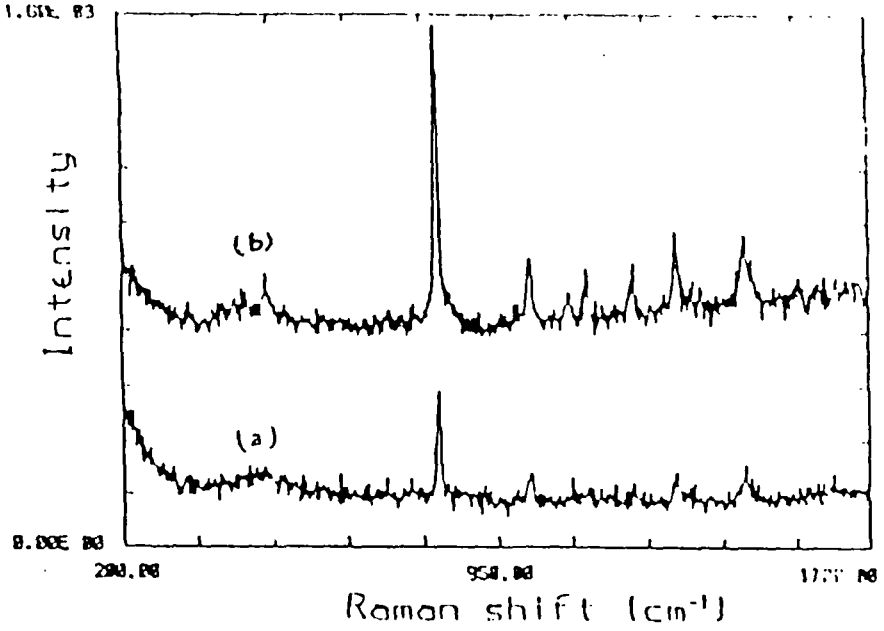

Fig. 4.3 : Raman spectra of (a) 0.98 M 1,4-dioxane aqueous solution; (b) SERS of 1.4-dioxane molecules with the same concentration adsorbed on α-Fe_2O_3 colloids (Reproduced from ref. 10

$NaBH_4$, at the ratio of 1 : 3 by volume Besides so many works with silver colloids, some scientists have made attempts to perform the SER study on gold, copper and iron sol also. Sánchez-Cortés and García-Ramos investigated the SERS of dimethylcytosine on both copper and silver sol [9]. Zhang et al [10] investigated the SERS of pyridine, 1,4 dioxane and 1-ethyl-3'-methyl-2-thiocyanine idodide molecules on α-Fe_2O_3 colloids. Figs. 4.2 and 4.3 have been reproduced from the refs. 9 and 10 for presentation.

4.4 Metal Island Films

Silver and indium island films had been used to record SERS spectra of copper and zinc phthalocyanine complexes [11,12]. Ritchie and Chen also investigated SERS from Ag island film substrate for benzoic acid and isonicotinic acid [13]. Thin Ag island films were prepared by evaporating the metal onto a tin oxide glass slide or sapphire substrate in a vacuum of 2×10^{-7} torr, at a rate of 0.2 to 0.4 Å per second. The films were then coated with copper and zinc phthalocyanine complexes in a vacuum system at a base pressure of 5×10^{-7} torr. The mass thickness of the film was monitored by a quartz crystal oscillator mounted close to the sample substrate. Metal thickness was about 7.5 nm on the substrates, and the analyte coating ranged from 7.5 to 200 nm. The films were then removed from the vacuum, immersed momentarily in an aqueous solution of molecules to be studied, rinsed with distilled water and air-dried. Fig. 4.4 shows the

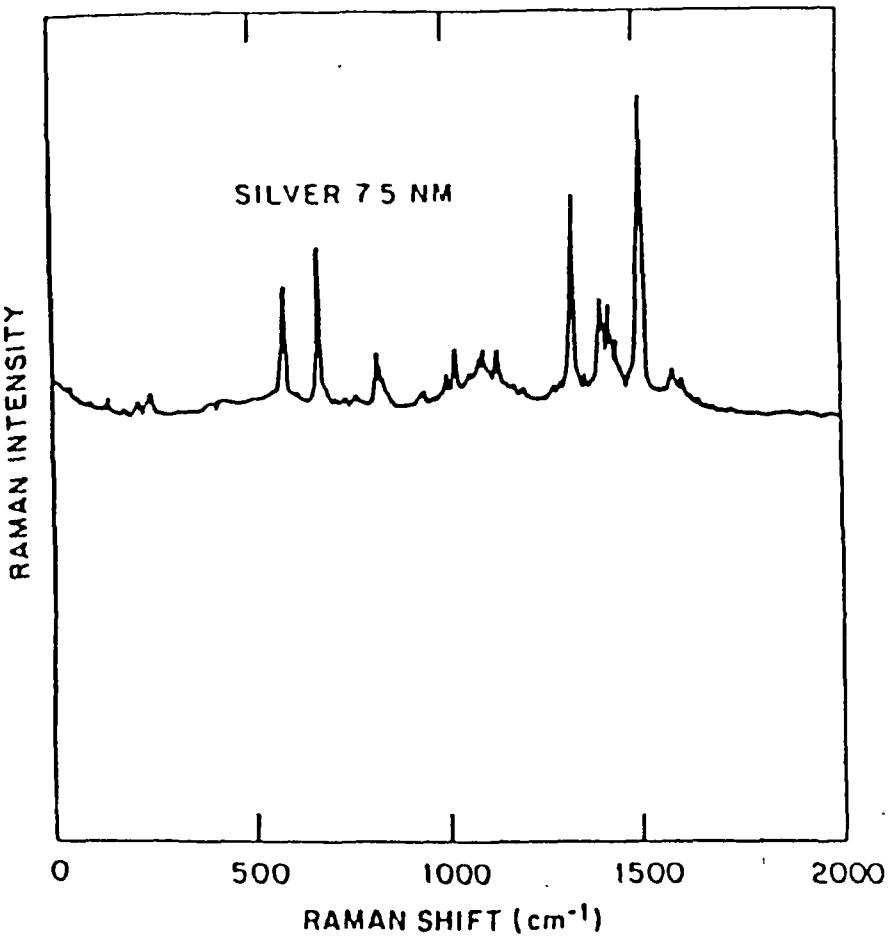

Fig. 4.4 : SERS spectrum of zinc phthalocyanine on silver island film

SERS spectrum of zinc phthalocyanine on 7.5 nm-thick silver island film recorded by Jennings et al [11]. The authors have also investigated the SERS of the same corresponding to a 25-nm film of zinc phthalocyanine. It was observed that the SERS signal from a 7.5 nm phthalocyanine film on silver under identical experimental conditions was comparable to a 25-nm film on silver, thus indicating that the SERS effect occurred with the first monolayer of adsorbate molecules. Figs. 4.5 and 4.6 show the SERS spectra of benzoic acid and isonicotinic acid adsorbed onto a 5 nm Ag island film substrate reproduced from the ref. 13).

4.5 Silver-Coated Microsphere Substrates

Let us take a suitable substrate like a cellulosic membrane, filter paper, glass plate or quartz material. Now, a 50 µl volume of a suspension of latex or teflon submioron spheres was applied to the surface of the substrate. The substrate was then placed on a high-speed spinning device and spun at 800 — 2000 rpm for about 20 s. The silver was deposited on the microsphere-coated substrate in a vacuum evaporator at a deposition rate of 2 nm/s. The thickness of the silver layer deposited was generally 50 — 100 nm. Fig. 4.7 shows the SERS spectrum of benzo[a]pyrene adsorbed on a silver-coated microsphere substrate [14]. The SERS-active substrate used in this study consisted of a microscope glass slide covered with

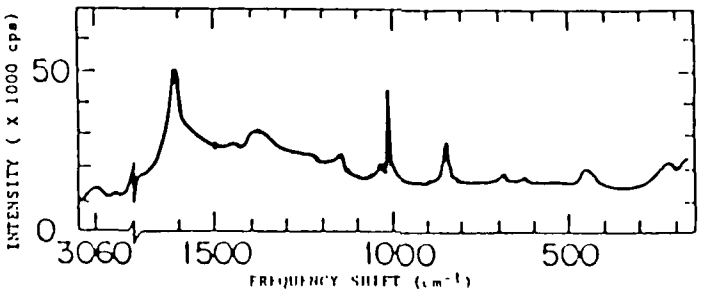

Fig. 4.5 : Raman spectrum for benzoic acid adsorbed onto a 50 Å Ag island substrate

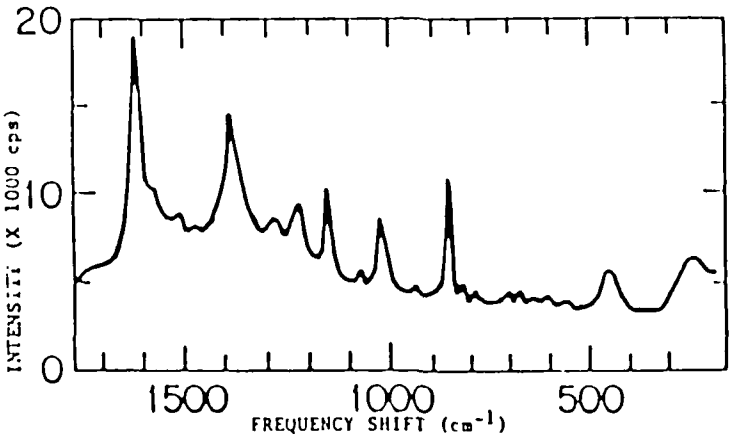

Fig. 4.6 : Raman spectrum for isonicotinic acid adsorbed at a 50 Å island film over layer

polystyrene microspheres having a 364 nm diameter and covered by a 75 nm thick layer of silver.

4.6 Silver-Coated Fumed Silica Substrates

Fumed silica-based substrate is quite SERS active and easy to prepare. Fumed silica has been used as a thickening agent in various industrial processes, including coating and cosmetics preparations. Fumed silica is manufactured in different grades, which vary with respect to surface area, particle diameter and degree of compression. In the preparation of SERS materials, the selection of the appropriate types of fumed silica is important. The fumed silica particles were suspended in a 10% water solution and were then coated onto a glass plate or filter paper. The substrate was then coated with a 50 -- 100 nm layer of silver by thermal evaporation. Now this substrate along with the fumed silica materials, which have submicron-size structure, provides the rough-surface effect for the SERS process. Fig. 4.8 shows an example of the SERS spectrum of a sample of phthalic acid (10^{-3}M) using the fumed silica-based substrate [15].

4.7 Silver-Coated Quartz Posts

Quartz posts of prolate spheroidal shape are prepared by a multistep operation. First, the quartz (SiO_2) should be plasma-etched with a silver island film as an etch mask [16-20].

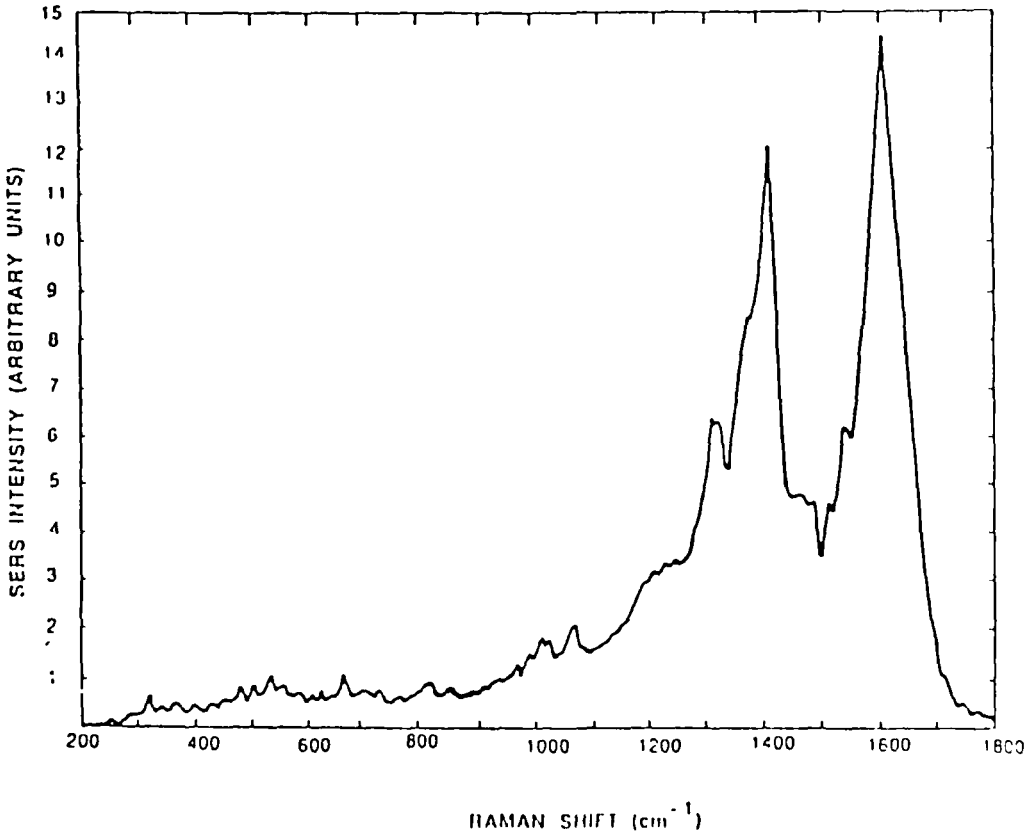

Fig. 4.7 : SERS spectrum of benzo[a]pyrene adsorbed on silver-coated microspheres substrate

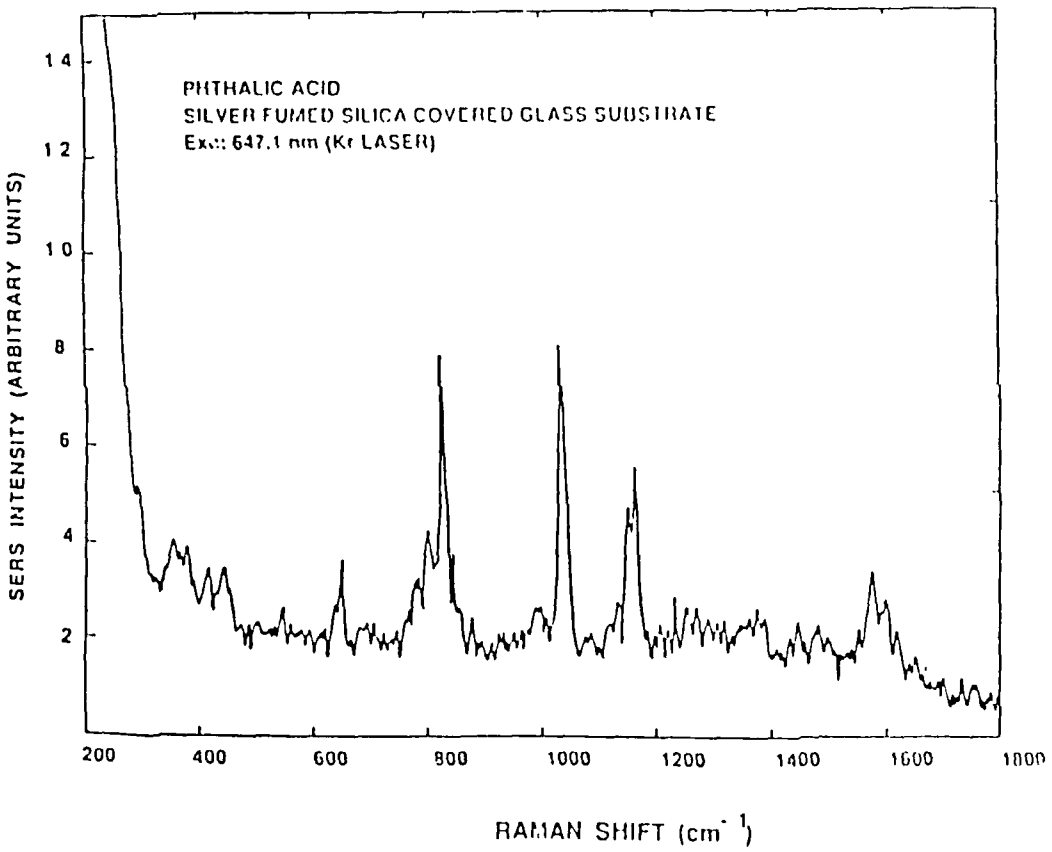

Fig. 4.8 : SERS spectrum of phthalic acid on silver-coated fumed substrate

Since fused quartz etches much more slowly than thermally deposited quartz, a 500 nm layer of SiO_2 was first thermally evaporated onto fused quartz at a rate of 0.1 - 0.2 nm/s. The resulting crystalline quartz was annealed to the fused quartz for 45 minute at approximately 950°C. A 5 nm silver layer was then evaporated onto the thermal SiO_2 layer, and the substrate was flash-heated for 20 s at 500°C. This heating causes the thin silver layer to bead up into small globules, which act as etch masks. The substrate was then etched for 30 - 60 min in a CHF_3 Plasma to produce submicron prolate SiO_2 posts, which were then coated with an 80 nm layer of silver at normal evaporation angle.

Enlow et al [19] have studied SERS of pyrene adsorbed on a silver-coated quartz post substrate. Fig. 4.9 shows the SERS spectrum of pyrene (reproduced from the ref. 19). The SERS spectrum of pyrene is similar to the NRS spectrum and exhibits a series of sharp peaks.

4.8 Metal-Coated Cellulose Substrates

A particular type of micropore filter paper coated with a thin layer of evaporated silver appear to provide an efficient SERS-active substrate. Scanning electron micrographs of this cellulosic material showed that this surface consists of fibrous 10 μm strands with numerous tendrils that provide the necessary microprotrusions required for the SERS enhancement. The simple

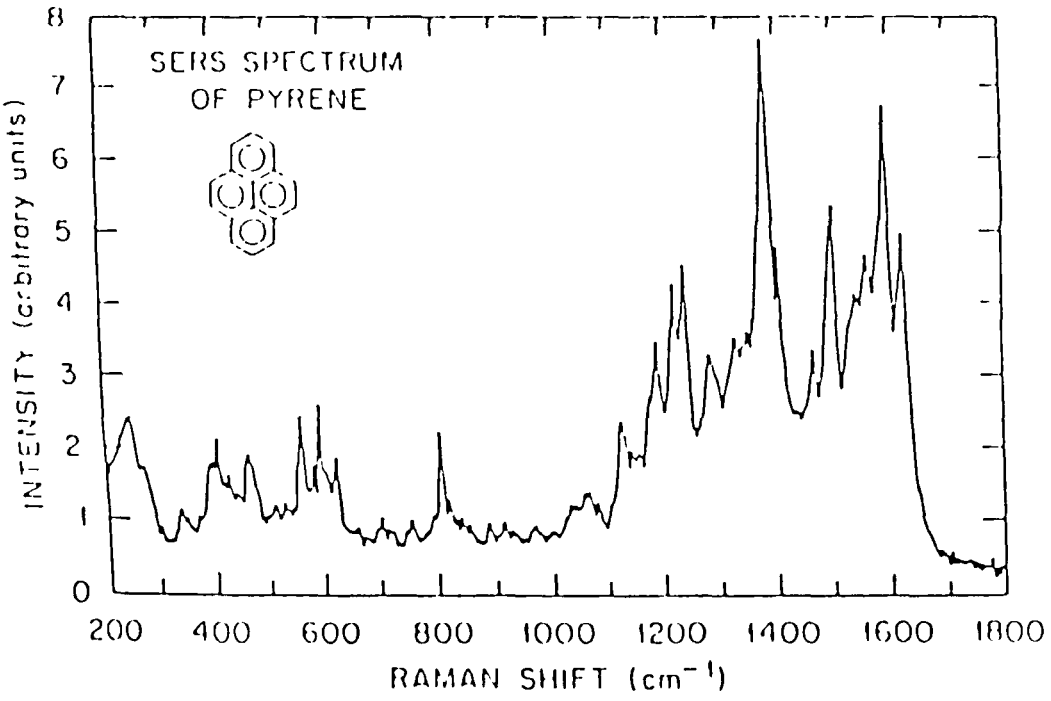

Fig. 4.9 : SERS spectrum of pyrene on a silver-coated quartz posts substrate.

technique employing silver-coated cellulose substrate was used to analyze benzo[a]pyrene DNA adducts [21]. The carcinogenic activity of benzo[a]pyrene (BP) in animals and its metabolic activation to the ultimate carcinogenic metabolite, BP-7, 8-diol-9, 10 epoxide [BPDE] hae been established [22,23]. Fig. 4.10 shows the SERS spectra of hydrolyzed products of BPDE-DNA adducts (8×10^{-6}M in 0.1 N HCl), BP-tetrol (10^{-4}M in methanol), and DNA (calf thymus DNA; 1.2 mg/ml in H_2O) [21].

4.9 Chemically Etched Metal Surfaces

Miller and his coworkers [24] furnished two simple etching procedures to make SERS-active copper surfaces. In the first procedure, copper foil was etched for 40 minute in 2 mol cm^{-3} nitric acid at room temperature. The second procedure consisted of sandblasting copper foil with alumina at 4 bar pressure and subsequently etching for 2 minute. An electron scanning micrograph of the metal surfaces indicated that both etching procedures could produce surface roughness on the range of 10 - 100 nm. These structures produce large electromagnetic fields on the surface when the incident photon energy is in resonance with localized surface plasmons. The etched SERS-active copper surfaces were used to investigate the SERS emission of a polycyclic aromatic dye, Nile blue. Fig. 4.11 (reproduced from ref. 24) shows the SERS spectrum of Nile blue adsorbed on a chemically etched copper surface using laser excitation at 662 nm.

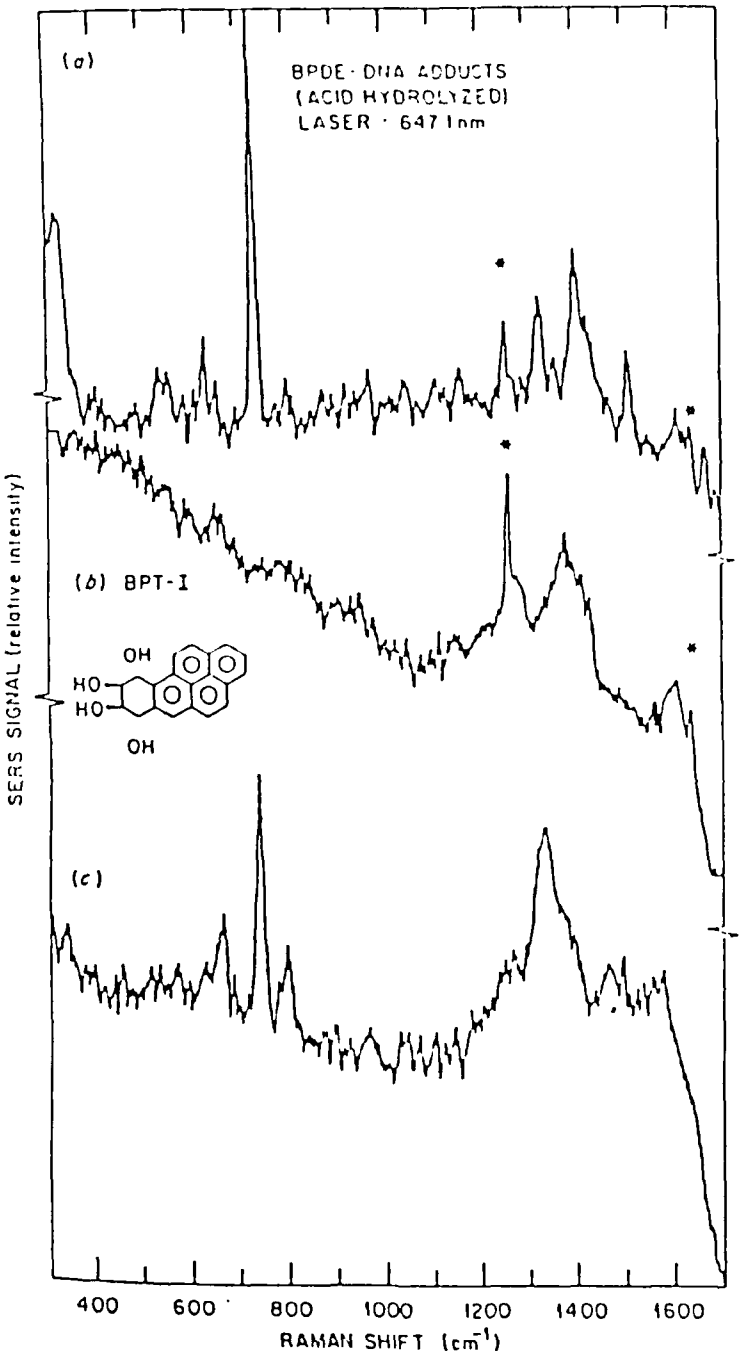

Fig. 4.10 : SERS spectra using silver-coated cellulose substrate : (a) BPDE adducts; (b) benzo[a]pyrene-tetrol-1; (c) calf thymus DNA.

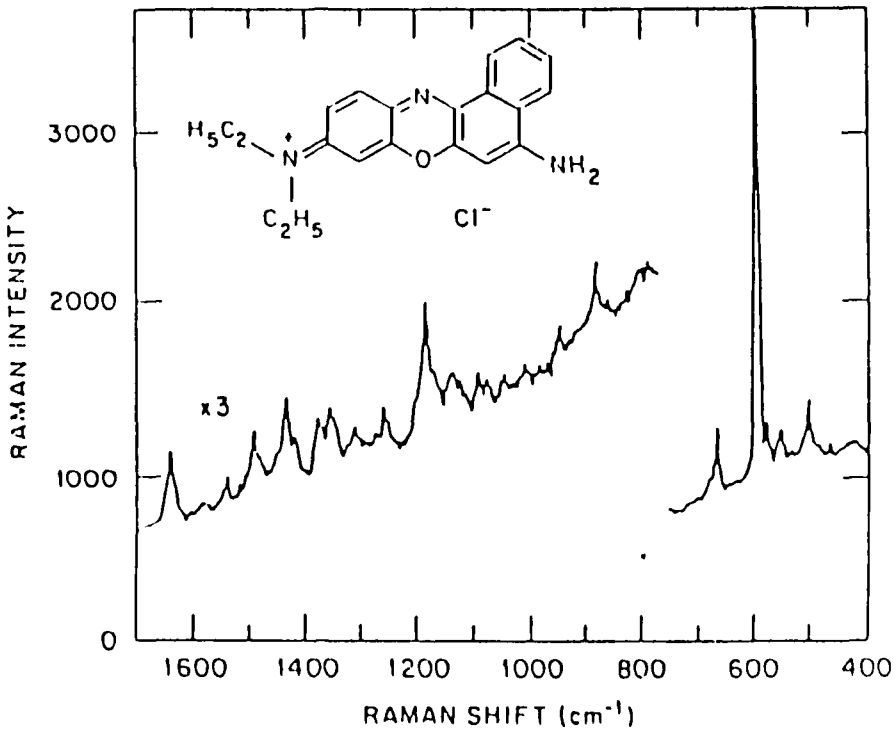

Fig. 4.11 : SERS spectrum of Nile blue on a sunblasted copper substrate etched for 70s.

4.10 Silver Membranes

T. Vo-Dinh et al [15] investigated the SERS on a simple type of solid substrate which was nothing but the silver membranes used for air particulate sampling. The filter already has micropores that provide the microstructure required to induce SERS. These substrates consist of silver membranes and can, therefore, be used directly as SERS-active substrates without requiring silver coating. Fig. 4.12 shows the SERS spectrum (reproduced from the ref. 12) of 1-nitropyrene adsorbed directly on a silver membrane. The silver membrane substrate was used directly as SERS substrate without requiring any chemical treatment or metal evaporation. The SERS spectrum of 1-nitropyrene obtained with the silver membrane is similar to that observed with the microsphere-coated substrates or the prolate quartz post substrates reported previously [19]. Although these substrates are simple to use and are commercially obtained, they are quite fragile and usually not as efficient as the above-mentioned substrates. Also, very often the silver surface of the membrane has to be freshly recoated in order to improve the SERS effect.

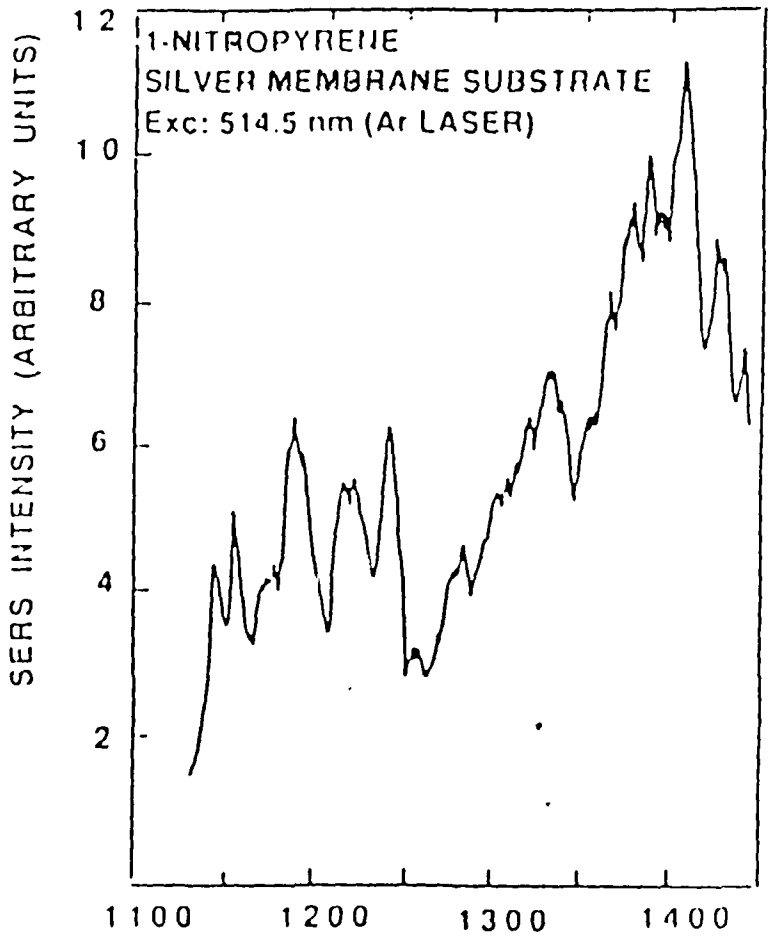

Fig. 4.12 : SERS spectrum of 1-nitropyrene adsorbed on silver membrane substrate.

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C H A P T E R - V

EXPERIMENTAL

5.1 ADSORPTION

5.2 COLLOIDAL SOLUTION

5.3 COLOUR OF A SOL

5.4 ELECTRICAL CHARGE OF THE COLLOIDAL PARTICLES

5.5 ADSORPTION BY COLLOIDS

5.6 ARGON ION LASER (Spectra Physics Model 171)

5.7 RAMANOR U1000 DOUBLE MONOCHROMATOR (Jobin Yvon)

a) Macrosample Chamber

b) Monochromator

REFERENCES

5.1 Adsorption

A 'surface' is nothing but the boundary or interface between the two media. Simply, we can also say that a 'surface' is that which separates two phases or material zones. Now, the process in which a layer of atoms or molecules of one substance forms on the surface of a solid or liquid, is called **adsorption.** All solid surfaces take up layers of gas from the surrounding atmosphere [1].

Le us consider two substances **A** and **B.** If the concentration of **A** on the surface of **B** is more than that in the bulk phase of **A,** then **A** is said to be adsorbed on **B.** In this case the concentration of **A** is quite high on the surface of **B** but it may be very low in the bulk of **B.** Here the substance **B** is called the **adsorbent** and the adsorbed substance **A** is called the **adsorbate.**

Adsorption is a surface phenomenon. The atoms on the rough surface of an adsorbent have unbalanced forces or even free valencies which can attach the adsorbate molecules. For instance, when a solid particle (which is placed within a gas or atmosphere) is broken into two, two new surfaces develop. The binding forces between the atoms that are separated by this process now become free. These forces act on molecules of gases present around the two particles. Similarly, when a solid in subdivided into a large number of particles, there will be a

large unbalanced force which can attach gas molecules from the surroundings. In the same way, when the solid particles are shaken with a solution they will take up **mo**lecules of the solute from it. This is the mystery behind the adsorption process.

Adsorption is of two tyes : **physical adsorption** or **physisorption** and **chemical adsorption** or **chemisorption.** If the adsorbate is held on the surface of the adsorbent by van der Walls' forces, the adsorption is called the **physisorption.** On the other hand, if the forces are nearly as strong as the chemical binding forces, the adsorption is called the **chemisorption** [2].

5.2 Colloidal Solution

A true solution is obtained if the common salt (NaCl) is dissolved in water. In a true solution, the solute particles are present as molecules or ions giving a homogeneous mixture which consists of a single phase. On the other hand, in a colloidal solution, the unit partcles of the dissolved substance are either very large molecules or essentially aggregate of a large number of molecules. These particles even though they may consist of thousands of molecules are too small to be seen under the optical microscope. Thus to the naked eye there could be no difference between a colloidal solution or an ordinary solution. However, if the colloidal particles grow in size further, they become visible under the microscope and then we get what we call a **suspension.**

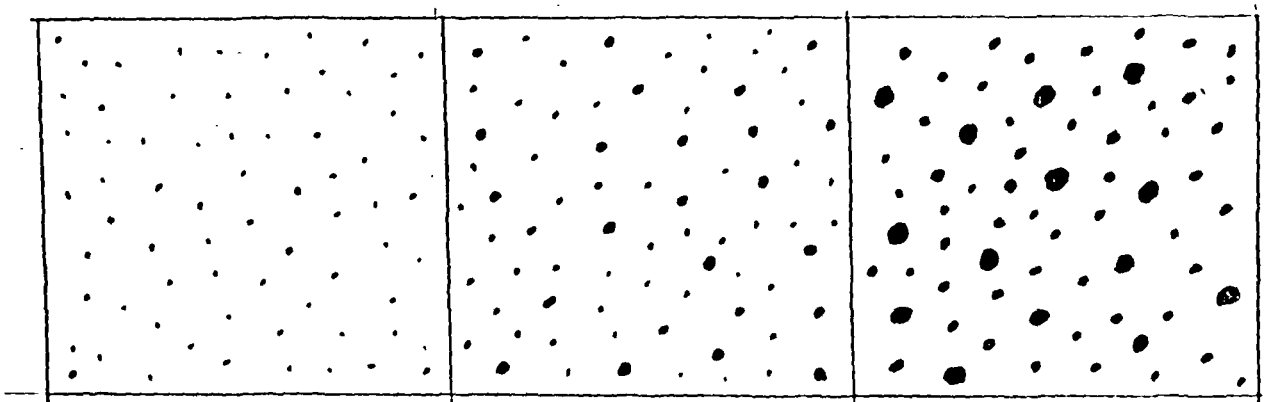
TRUE SOLUTION
Particle diameter:
0.1 nm-5 nm.
COLLOIDAL SOLUTION
Particle diameter:
5 nm-200 nm.
SUSPENSION
Particle diameter:
200 nm-50,000 nm.

Fig. 5.1

So, we can say that a **colloid** is a state of matter intermediate between a solution and suspension. Because of the small particle size the colloidal solution frequently appears homogeneous to the naked eye although their heterogeneity may be demonstrated by looking under an ultra-microscope. Unlike suspensions colloidal particles do not settle down on standing and are not separable by ordinary filtration.

The Fig. 5.1 shows the size of the particles in solution, colloid and suspension. The particles in a colloidal solution is called **dispersion phase** and the solvent medium is called the **dispersion medium** with solid particles of sub-microscopic size (diameter < 100 nm) the dispersion is called a **sol** [3]. Depending upon the disperse phase and dispersion medium there may be eight types of colloidal solutions :

Dispersive phase	**Dispersion medium**	**Designation**	**Examples**
Gas	Liqu id	Foam	Soap, Lather.
Gas	Solid	Solid foam	Sponge
Liquid	Gas	Aerosol	Fog, sprays.
Liquid	Liquid	Emulsion	Milk
Liquid	Solid	Gel	Jellies
Solid	Liquid	Sol	Silver sol
Solid	Solid	Solid sol	Ruby, gem stones.
solid	Gas	Aerosol	Smoke, mist.

5.3 Colour of a Sol

The colour of a sol depends upon the followings :

(i) The size and shape of particles.

(ii) The specific selective absorption power of the dispersed phase and the dispersion medium.

(iii) The wavelength of the light falling on it.

(iv) The way an observer receives the light, e.g., whether by transmission or reflection.

For example, during the change of yellow colour of silver sol to blue, the size of the particles increases.

5.4 Electrical Charge of the Colloidal Particles

Colloidal particles almost invariably carry positive or negative charge and all particles of a given sol carry the same charge [4]. For example, silver sol is negatively charged while ferric hydroxide sol is positively charged. The charge on the particles may due to one or more of the following causes :

(i) Due to the dissociation of the surface molecules.

(ii) Due to the dissociation of molecules adsorbed on the surface.

(iii) Due to preferential adsorption of ions.

(iv) Due to the electrification of particles by friction.

(v) Due to electron capture by the sol particles.

(vi) Due to the presence of some acidic or basic groups.

5.5 Adsorption by Colloids

In a colloidal solution a very small mass of the dispersed phase is present as a very large number of tiny particles. Thus the area of the surface of this phase is very large relative to the mass of the substance. Moreover when we break a substance into small particles the valencies of the separating atoms which were mutually satisfied are now set free. The large surface offered by colloidal particles and these free valencies are responsible for marked adsorption by colloids.

5.6 Argon Ion Laser (Spectra Physics Model 171)

The argon ion laser is a class of gas lasers that produce continuous wave (CW) output and have high plasma temperatures. The energy level diagram of singlylonized argon is shown in Fig. 5.2. It can be assumed that the two ground state sublevels of the $4s^2P$ state that constitute the two lower states for all of the argon ion laser transitions have very short lifetimes and very high probabilities of emitting energy and dropping to the argon ion ground state. The energy separation between the lower laser levels and the ground state of the ion is very large, so that, even though the plasma is at high temperature, there is no tendency for a Boltzmann population

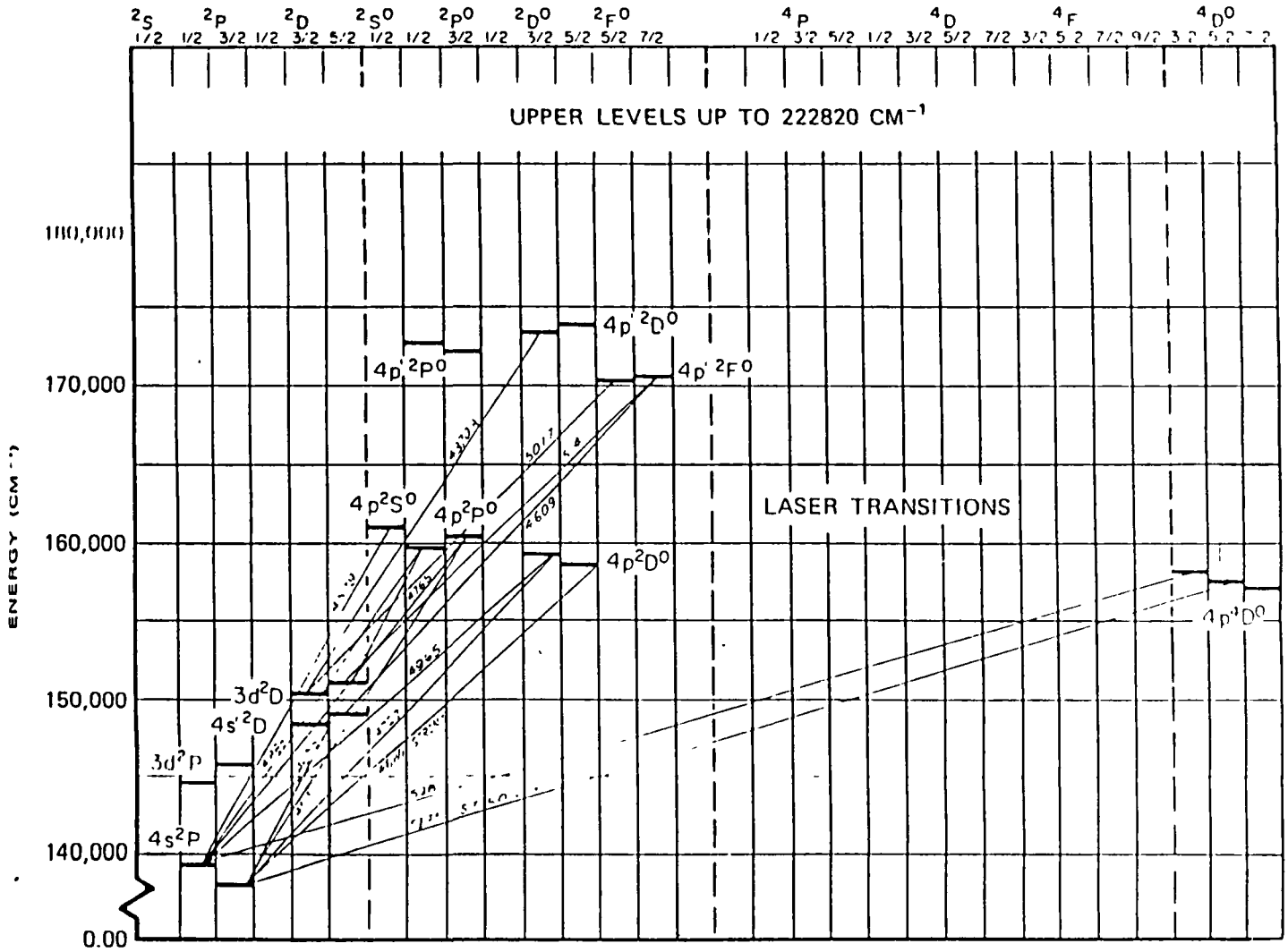

Fig. 5.2 : Argon ion laser transition

equilibrium to be established between the ionic ground state and the lower laser levels.

The Model 171 offers a number of available wavelengths at 514.5 nm, 501.7 nm, 496.5 nm, 488.0 nm, 472.7 nm, 465.8 nm and 457.9 nm. Among these 488.0 nm and 514.5 nm lines are strong [5].

The Model 171 requires water for cooling its transistor pass bank, magnetic field solenoid, and plasma tube. The cooling system is designed (Fig.5.3) to operate with input water temperature as high as 35°C and requires a flow rate of 0.22 liters/sec (3.5 gallons per minute) at a differential pressure of 450 KN/m^2 (46 Kg/cm^2, 65 Psi) when operating at full power.

A magnetic field is generated by a solenoid surrounding the plasma tube. It tends to force the electrons away from the walls of the tube. Since the electrons are not lost as quickly to the walls, there is a shift of energy distribution of the free electrons towards higher values. The atomic levels can only be populated through collisions with electrons having at least the energy of the state being excited. Therefore, the result of the magnetic field is a stronger population inversion.

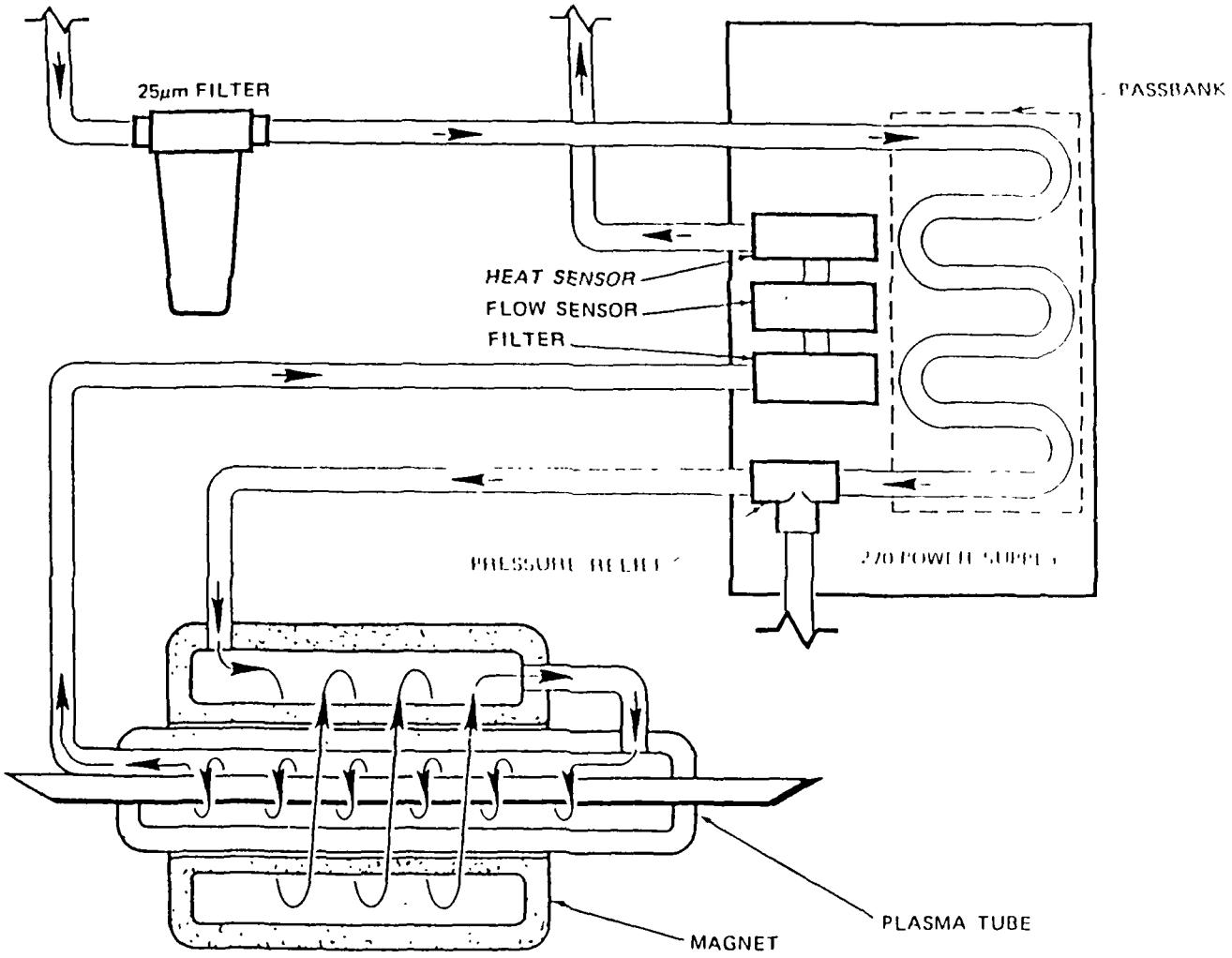

Fig. 5.3 : Cooling arrangement for the transistor pass bank, plasma tube and solenoid.

5.7 RAMANOR U1000 Double Monochromator (Jobin Yvon)

(a) Macrosample Chamber

Laser beam enters into the macro sample compartment as shown in Fig.5.4 through accessory support which includes half wave plate **1**, interference filter and laser shutter **2**. Laser shutter is controlled by scan controller. It prevents blinding the detector with the excitation line $\bar{\nu}_o$. The shutter closes automatically at the chosen value $\Delta\nu$ and remains closed between $\bar{\nu}_o - \Delta\bar{\nu}$ and $\bar{\nu}_o + \Delta\bar{\nu}$. **3a** and **3b** are collimating mirrors which correct the alignment of incident laser beam in relation to sample compartment axis. Laser beam focussing lens **4** adjusts convergence of beam on the sample. The sample holder **5** have XYZ orientation to place sample in optimum position. Raman light is collected by Benoist-Berthiot f/1.8 collecting lens having 80 mm focal lenth with translation adjustment [6]. Lens adjustment knob **7** is required to adjust the height of the collecting lens. Perfect adjustment of spherical mirrors **8** considerably increases intensity of lines with transparent sample. The sample compartment is attached to the monochromator by the accessory holder. The monochromator has four fixation holes for this connection.

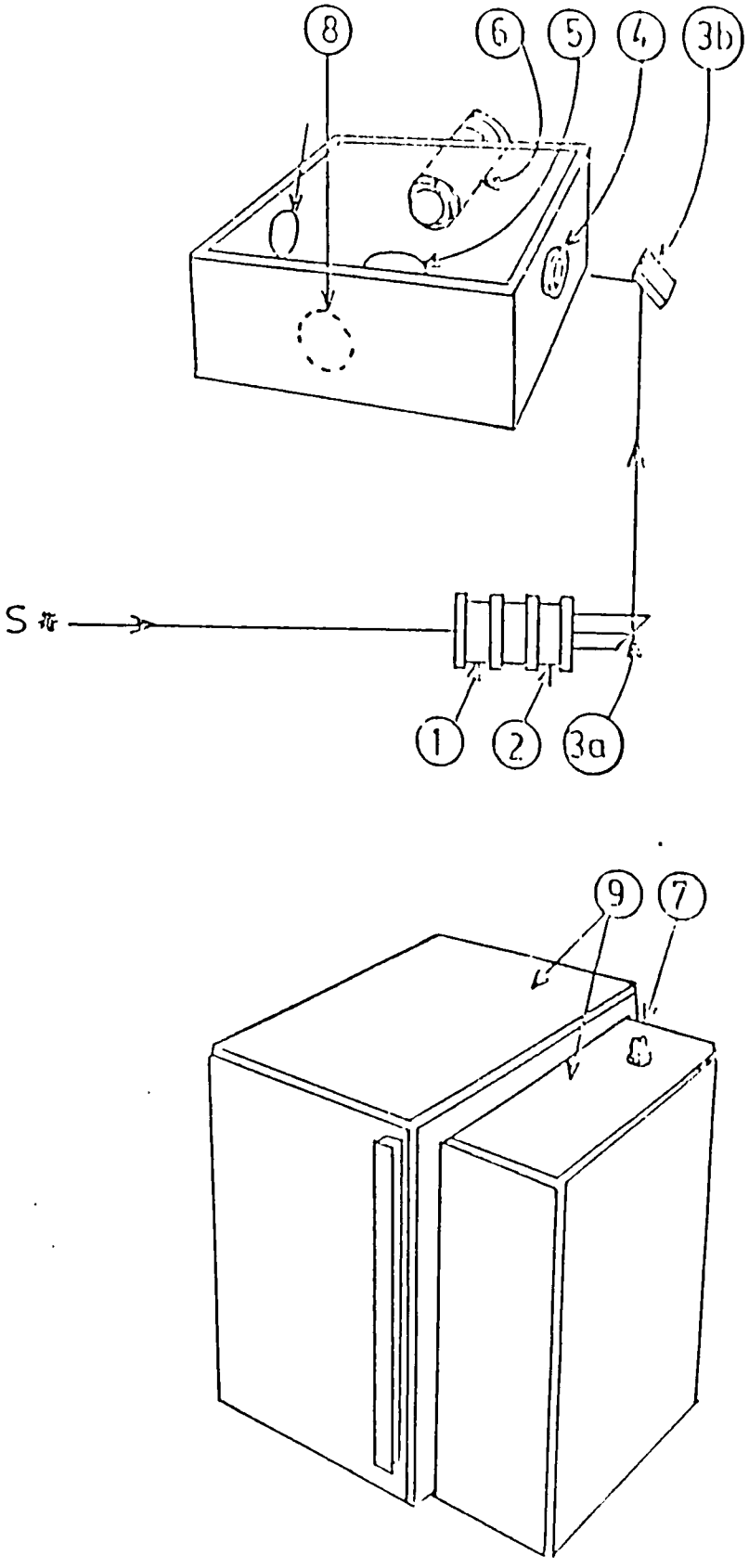

Fig. 5.4 : Sample compartment

(b) Monochromator

For intensity measurements in spectra we need to separate out a narrow range of the spectrum at a time. In principle this can be done in any spectrograph by replacing the photographic plate with a narrow slit whose length is parallel to the spectral lines. That would make the spectrograph a monochromator.

The RAMANOR U1000 is a double monochromator designed for spectroscopic applications that require high resolution and extreme stray light rejection. The main components of the RAMANOR U1000 are two identical monochromators in an additive mount equipped with plane holographic gratings (R_1 and R_2). The holographic gratings having 1800 grooves/mm in the standard version but any number of grooves/mm may be installed with the U1000. Each monochromator features an assymetric Czerny-Turner mounting equipped with two slits which open symetrically [7]. The two gratings are mounted and rotate on a single horizontal shaft which is parallel to the grating grooves. There are four slits F_1, F_2, F_3 and F_4. The slits straight and horizontal are mounted in a plane parallel to the rotation axis. The horizontal slit configuration is highly advantageous to the RAMANOR U1000 for work performed on liquid samples. MC_1, MC_2, MC_4 and MC_5 are collimating mirrors.

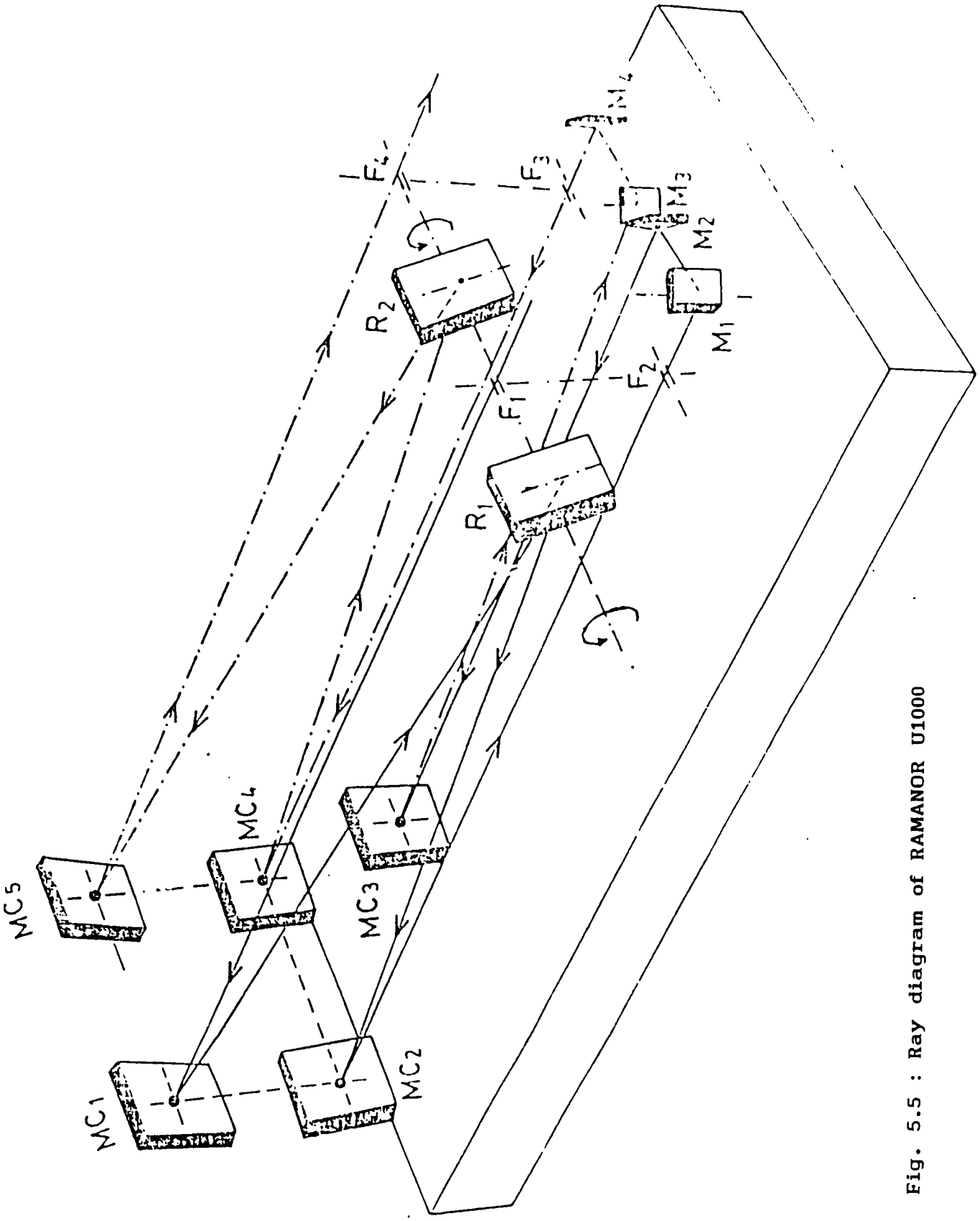

Fig. 5.5 : Ray diagram of RAMANOR U1000

Raman light collected by collecting lens, enters monochromator through slit F_1 (kept at 100 μ) fall on collimating mirror MC_1 and then on holographic grating (R_1) and diffracted light fall on collimating mirror MC_2. The optical path is diverted by mirrors M_1, M_2, M_3 and M_4. The exit slit F_2 (100 μ) of the first monochromator is imaged on the entrance slit F_3 (200 μ) of the second monochromator by means of the coupling concave mirror MC_3 with the focal length of 0.5 m. Raman light enters second monochromator through slit F_3 which have collimating mirrors MC_4, MC_5 and holographic grating R_2 and comes out through exit slit F_4. After that it enters into photomultiplier tube (cooled with water current) for detection which is recorded by X-Y recorder.

The wavenumber scanning is controlled by the microprocessor scan controller Spectra Link including the following :

(i) Absolute or relative wavenumber display.

(ii) Wavenumber scan speed selector in cm^{-1}/min.

(iii) Repetitive scan.

(iv) Recorder control.

(v) Laser shuter control.

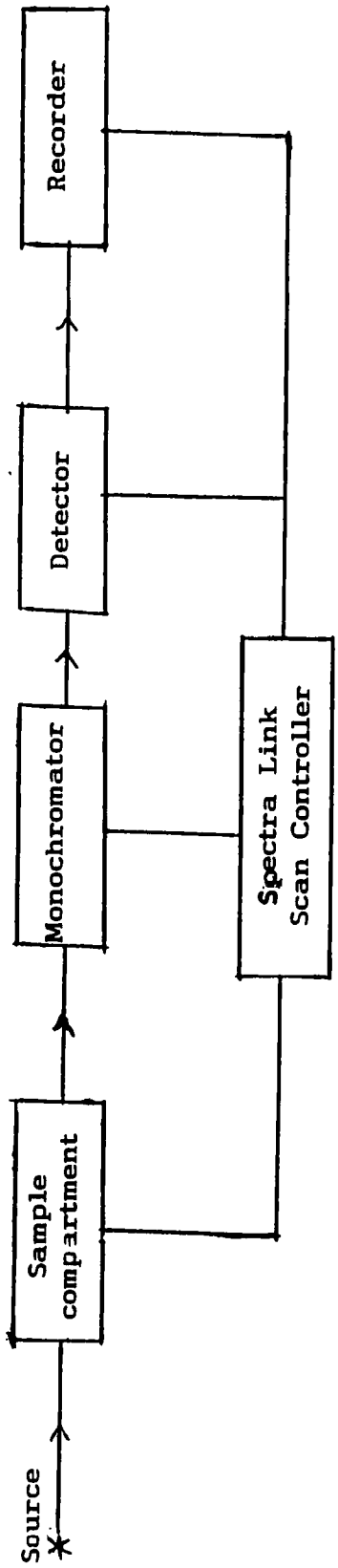

Fig. 5.6 : Block diagram of Laser Raman Spectrometer.

RAMANOR U1000 double beam monochromator have the following specifications :

Grating size : 110 x 110 mm^2

Number of grooves : 1800/mm

Rosolution : 0.15 cm^{-1} on the Hg line at 5791 Å

Dispersion : 9.2 cm^{-1}/mm at 514.5 nm.

Stray light rejection : 10^{-14} at 20 cm^{-1} from the Rayleigh line.

Scanning speed : 0.1 to 4800 cm^{-1}/min.

Wavenumber accuracy : $\pm$ 1 cm^{-1} over 5000 cm^{-1}

Slit width : 0 - 3 mm.

Slit height : 0 - 30 mm.

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C H A P T E R - VI

SURFACE ENHANCED RAMAN SCATTERING (SERS) INVESTIGATIONS OF 2-, 3- AND 4-METHYLPYRIDINES ADSORBED ON SILVER SOL

6.1 INTRODUCTION

Surface-enhanced Raman scattering (SERS) spectroscopy has been established as a powerful method for elucidating the structure of adsorbed molecules and their interactions with the surfaces [1,2]. Intense Raman signals are obtained from rough metal surfaces, periodic metal structures such as gratings, lithographically produced small spheroids, island films and colloidal particles. Subsequent development of SERS [3,4,5] has made possible the scientific inquiry of various interfacial porcesses that were previously intractable. Moreover, the fluorescence background which prevents observations of Raman spectra may frequently be reduced owing to the interaction between the adsorbates and the surfaces [6,7]. Research in the field of SERS has significantly broadened in scope to encompass additional phenomena such as second harmonic generation [7,8,9], hyper Raman scattering [10,11] and their resonant analogue.

Since the discovery of SERS by Fleischmann et al [12] there have been a tremendous growth in research activities directed towards understnading the underlying origin of giant enhancement ($\approx 10^6$) in the Raman scattering efficiency. It is by now generally accepted that only two broad classes of contributions attribute to the observed enhancement [3,13,14] in SERS : electromagnetic and chemical. The electromagnetic theory ascribe the enhancement to the presence of surface plasmons in

the metal substrate. The chemical theory asserts that a dynamical charge transfer excitation of an electron from the metal to the adsorbed molecule gives rise to a resonance effect in the Raman cross-section of the molecule. SERS study of methylpyridines have been performed by Bunding et al [15] using silver electrode method. The competitive adsorption of 2-and 4-methylpyridines on a polycrystalline Ag-electrode was studied by Sato et al [16]. The present SERS studies of 2-, 3-and 4-methylpyridines have been performed using silver sol technique and the spectral findings have been explained in the light of current SERS theories.

6.2 EXPERIMENTAL

6.2.1 Materials

2-Methylpyridine (Fluka, Switzerland), 3-methypyridine (Aldrich, U.S.A) and 4-methylpyridine (Aldrich, U.S.A) were of the highest grade commercially available and were used without further purification. Silver nitrate and sodium borohydride were of analytical grade and obtained from the Sigma Chemicals (U.S.A.). Water was deionized and triply distilled.

6.2.2 Preparation of Silver Sol

The aqueous silver sol used in these experiments was prepared from a recipe described by Creighton et al [17]. 20 ml

of 1.0×10^{-3}M aqueous solution of *silver nitrate* was added with 60 ml of 2.0×10^{-3}M aqueous solution of *sodium borohydride* with uniform stirring. Both the solutions have been chilled to ice-temperature before hand. A light yellow coloured Ag sol thus obtained was stable for a few months. The pH paper was used to check the approximate pH of the sol and was found to be in between 7 and 8.

6.2.3 **Instrumentation**

The UV/VIS absorption spectra of the silver sol were recorded on a Spectronic 1001 (Milton Roy, Japan) absorption spectrophotometer using cells of 1 cm thickness. Raman scattered light was analyzed with a Ramanor U1000 (Jobin Yvon, France) double monochromator equipped with 1800 grooves/mm holographic gratings, followed by a thermoelectrically cooled RCA/C 31034 photomultiplier tube. The 514.5 nm exciting line was employed from an Ar^+ laser with a typical laser power of approximately 100 mW at the sample. Samples were contained in glass capillary tubes and the scattered light was collected 90° to the incident laser beam. The peak positions of sharp bands are accurate to within $\pm 2\ cm^{-1}$.

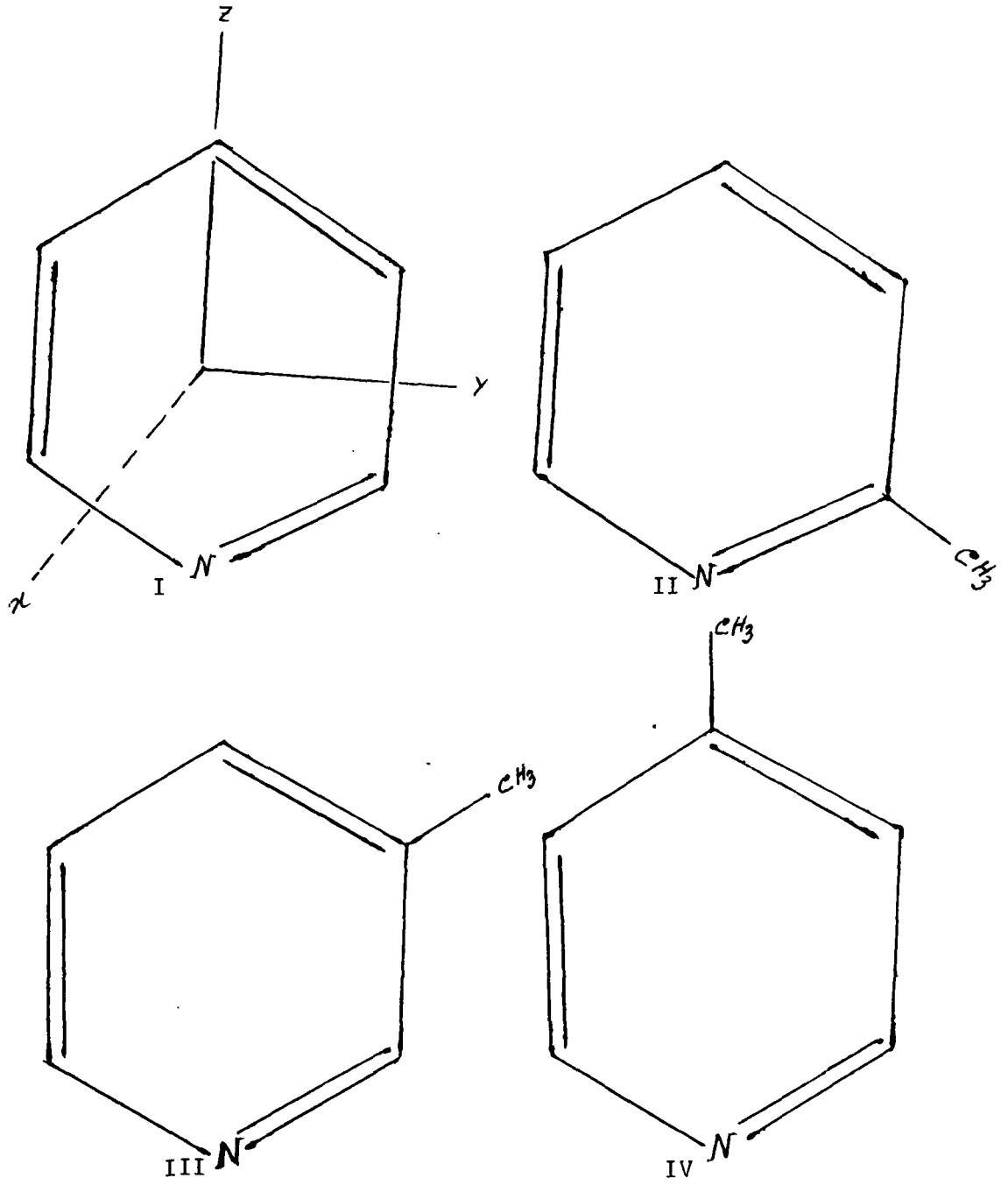

Fig. 6.1 : Structure of I. Pyridine; II. 2-methylpyridine; III. 3-methylpyridine; IV. 4-methylpyridine.

6.3 RESULTS AND DISCUSSIONS

Fig. 6.2a shows the absorption spectrum of the freshly prepared Ag sol. It has an extinction band at 390 nm which is the characteristic of the sol particles being almost spherical in shape with diameter in the range 1 - 50 nm [18,19]. Light absorption by the silver particle induces this extinction band which is attributed to the excitation of plasma vibrations in the limited electron gas of the particles [20]. After the addition of 2-methylpyridine in the sol, the colour of the sol gets changed and the extinction band shifts to 412 nm (Fig. 6.2b) which indicates the growing of the particles' size due to small aggregation (but not precipitation) of the sol particles after adsorbing 2 MP molecules. Similar phenomena have been observed after the addition of 3- and 4-methylpyridine in the silver sol.

6.3.1 2-Methylpyridine

2-Methylpyridine (2MP) molecule possesses C_s symmetry and the structure of this molecule has been shown in Fig. 6.1. The normal Raman (NR) spectrum of 2MP solution (Conc. 0.1M) is shown in Fig. 6.3(a) and SERS spectrum of 2MP adsorbed on silver sol (2MP conc. 1.0×10^{-5}M) has been shown in Fig. 6.3(b). Table 6.1 contains the vibrational frequencies, assignments and absolute enhancement factors for the various NR and SERS bands. In the table the species a' and a" designate

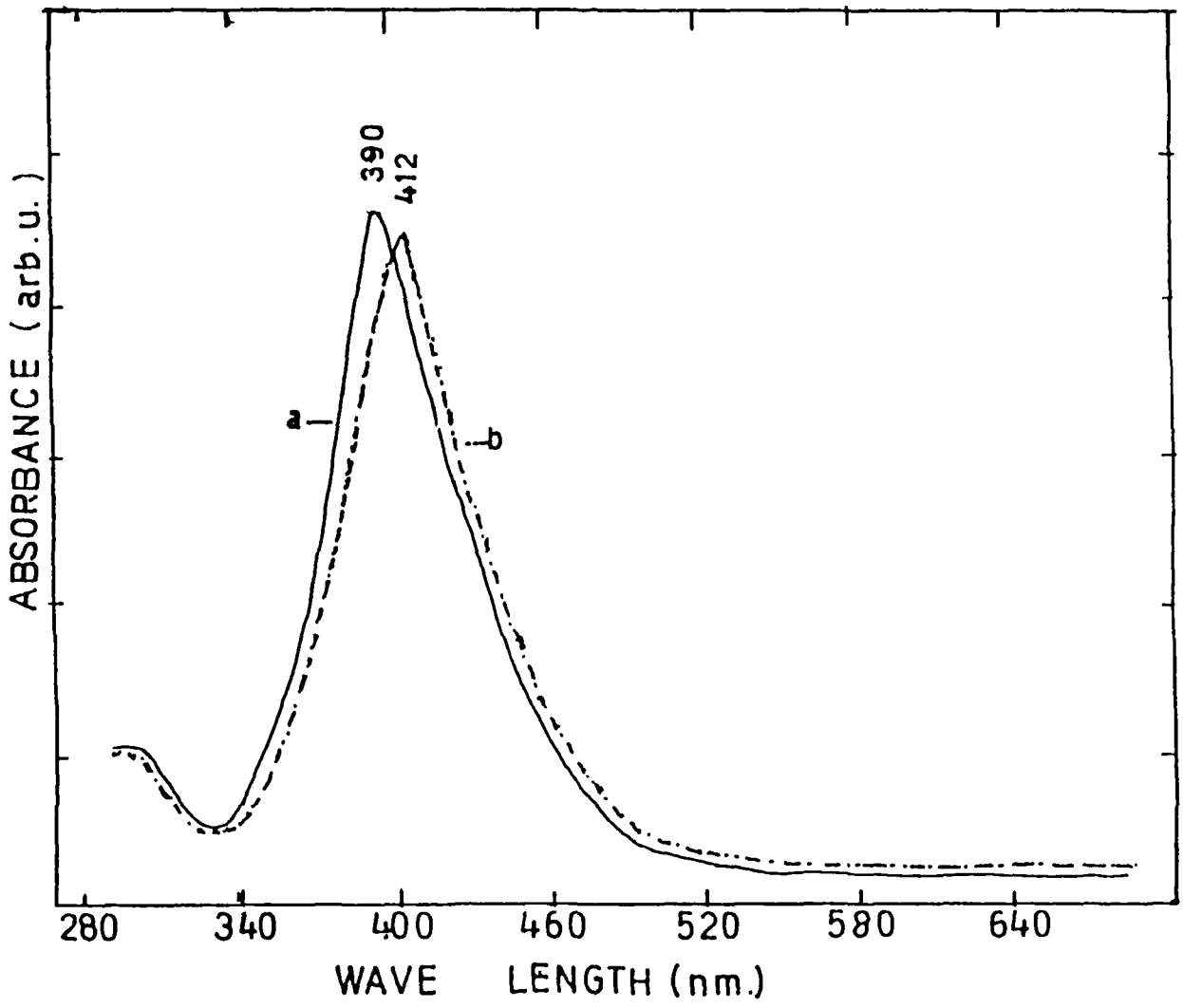

Fig. 6.2 : Absorption spectrum of (a) freshly prepared Ag sol, (b) after addition of 2-methylpyridine in the sol.

the in-plane and out-of-plane vibrations respectively. 'M' signifies the internal methyl group vibrations whereas 'm' stands for the carbon-methyl vibrations.

The ring breathing mode ν_1 (Wilson mode 1) at 1006 cm^{-1} in the NR spectrum has been shifted to higher frequency at 1022 cm^{-1} in the SERS. This shift of the ring breathing mode to higher frequency implies, according to Furukawa et al [21], that the molecules have been adsorbed on the surface of the silver (Ag) sol particles through the ring N-atom. The ring deformation and ring stretching modes ν_{16a}, ν_{6a}, ν_{6b}, ν_4, ν_{12} and ν_{8b} at 410, 550, 676, 726, 800 and 1574 cm^{-1} in the ordinary Raman spectrum correlate, respectively, with the bands at 420, 558, 704, 726, 810 and 1580 cm^{-1} in the SERS spectrum All these modes are blue-shifted (except the mode ν_4 at 726 cm^{-1}). The blue-shift of these ring modes also indicates the formation of Ag-N bond as it limits the freedom of deformation of some of the modes. The formation of Ag-N bond is preceeded by chemisorption. The chemisorption of a molecule on the silver surface is accompanied by an electronic transition associated with charge transfer from the metal to the molecule giving rise to a resonance effect in the Raman cross section of the adsorbed molecule.

The absolute enhancement factor for various bands have been estimated by the method used by Kerker et al [22] i.e.

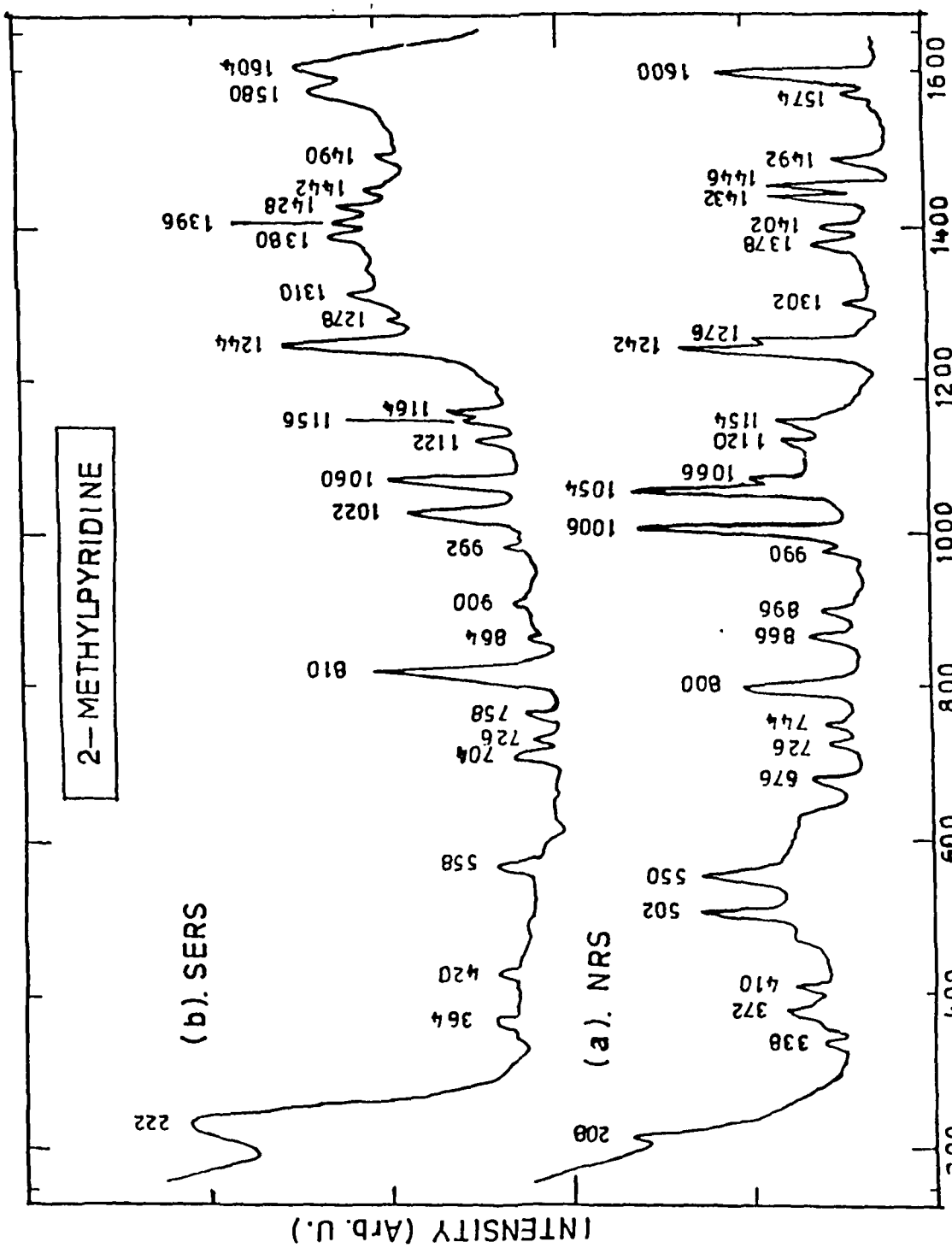

Fig. 6.3 : (a) Normal Raman Spectrum (NRS) of 2-methylpyridine solution (conc. 0.1 M) (b) SERS spectrum of 2-methylpyridine adsorbed on silver sol (overall conc 1.0×10^{-5}M). Laser power 100 mW (at the sample); Scan Inc. 2 cm^{-1}/step, FS CNT 3000, PMT volt 1250.

TABLE 6.1 : Observed NRS and SERS bands of 2-methylpyridine

Wilson mode	Species	NRS (cm^{-1})	SERS (cm^{-1})	Enh. factors	Assignments
m_3	-	208	222	1.2×10^6	C-CH_3 o.p.b.
15	a'	338	-	-	C-H i.p.b. X-sensitive
m_2	-	372	364	5.0×10^3	C-CH_3 i.p.b.
16a	a"	410	420	6.0×10^3	C-C o.p.b.
11	a"	502	-	-	C-H o.p.b.
6a	a'	550	558	8.0×10^3	C-C i.p.b. X-sensitive
6b	a'	676	704	1.5×10^4	C-C i.p.b.
4	a"	726	726	1.0×10^4	C-C o.p.b.
10b	a"	744	758	1.4×10^4	C-H o.p.b.
12	a'	800	810	2.5×10^4	C-C i.p.b. X-sensitive
10a	a"	866	864	8.0×10^2	C-H o.p.b.
5	a"	896	900	7.6×10^3	C-H o.p.b.
17a	a"	990	992	7.0×10^3	C-H o.p.b.
1	a'	1006	1022	1.2×10^4	Ring breathing
$M_6(b_1)$	-	1054	1060	8.5×10^3	CH_3 i.p.wag.
18a	a'	1066	-	-	C-H i.p.b.
18b	a'	1120	1122	1.3×10^4	C-H i.p.b.
9a	a'	1154	1156	6.0×10^3	C-H i.p.b.
$M_6(b_2)$	-	-	1164	-	CH_3 o.p.wag.
m_1	-	1242	1244	1.4×10^4	C-CH_3 str.
-	-	1276	1278	1.0×10^2	866+410=1276 combination band
3	a'	1302	1310	1.1×10^4	C-H i.p.b.
14	a'	1378	1380	9.0×10^3	C-C,C-N str.
M_3	-	1402	1396	9.1×10^3	HCH sym.angle deform.
$M_4(b_2)$	-	1432	1428	4.0×10^3	HCH assym.angle deform.
$M_4(b_1)$	-	1446	1442	3.8×10^2	HCH assym.angle deform.
19a	a'	1492	1490	7.0×10^3	C-C,C-N str.
8b	a'	1574	1580	9.4×10^4	C-C str.
8a	a'	1600	1604	2.0×10^4	C-C str.

a) The normal Raman (NR) frequencies of the present work are comparable to the assignment of Green et al [28].

b) i.p.b = in-plane bending, o.p.b = out-of plane bending, str = stretching.

$$\text{Abs. Enh.} = \frac{\text{Area of a particular band in SERS}}{\text{Area of the same band in NRS}} \times \frac{\text{Conc. of the sample in soln.}}{\text{Conc. of the sample in sol.}}$$

In the Table 6.1 it can be found that, among the fundamentals, the in-plane bending modes 12, 18b and 6b have been enhanced more in comparison to the out-of-plane bending modes. This is in accordance with the suggestion of Creighton [23] for the 'standing-up' orientation of the adsorbed molecule. Creighton suggested that if the molecule adsorbed on 'standing-up' fashion (i.e. the plane of the molecule is perpendicular to the surface) the in-plane vibrational modes will be enhanced more. It should be mentioned that the large enhancement for this in-plane vibrations have been attributed to the electromagnetic contribution of the origin of SERS phenomenon and the shift of band positions of some modes and their enhancement may be accounted for the chemical effect of the SERS process.

6.3.2 **3-Methylpyridine**

3-Methylpyridine (3MP) molecule is also having the C_s symmetry as 2MP and the structure is shown in Fig. 6.1.
Fig. 6.4(a) shows the normal Raman (NR) spectrum of 3MP solution (conc 0.1M) and the Fig. 6.4(b) is the SERS spectrum of 3MP in silver sol (3MP conc. 1.0×10^{-5}M). The vibrational frequencies, assignments and absolute enhancement factors for the various NR and SERS bands have been tabulated in Table 6.2.

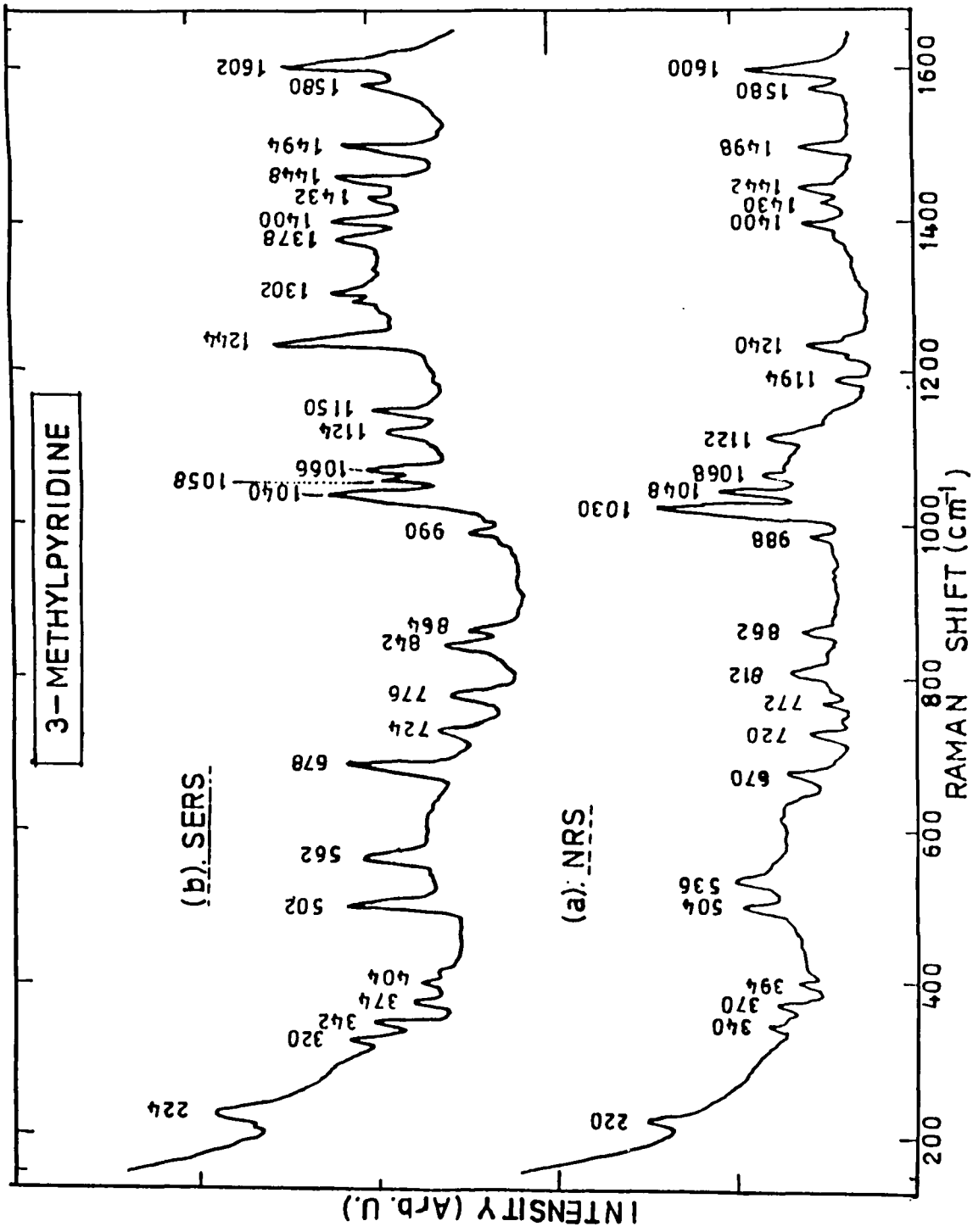

Fig. 6.4 : (a) Normal Raman Spectrum (NRS) of 3-methylpyridine solution (conc. 0.1 M)
(b) SERS spectrum of 3-methylpyridine adsorbed on silver sol (overall conc. 1.0×10^{-5}M). Laser power 100 mW (at the sample); Scan Inc. 2 cm^{-1}/step, FS CNT 3000, PMT volt 1250.

The ring deformation modes 16a, 6a, 6b, 4 and 12 have been shifted to higher frequency by 10, 26, 8, 4 and 30 cm^{-1} respectively. This shift of the ring bending modes indicates, as stated earlier (i.e. for 2MP), the formation of Ag-N bond between the 3MP molecule and the Ag surface. It has also been observed that the ring breathing mode 1 is blue-shifted in the SERS spectrum by 10 cm^{-1}. This is also consistent with the formation of a chemical bond between the silver surface and the ring N-atom of the molecule [21]. Again, if we consider the enhancement criteria, it can be found, in the Table 6.2, that the in-plane vibrational modes have been enhanced more (even of the order of 10^5). This is also an additonal indication of forming Ag-N bond and taking-up the 'standing-up' orientation of the adsorbed molecule [23]. According to Creightons' suggestion, it is known that for 'standing-up' orientation,
$a' > a''$. In the present observation these conditions are being satisfied. So, it appears that the adsorbed 3MP molecule takes-up the 'standing-up' position on the surface of the sol particles. Finally, the presence of Ag-N bond has been confirmed by the appearance of the band at 320 cm^{-1} in the SERS spectrum of 3MP as this band is being assigned to be the Ag-N stretching band [24].

TABLE 6.2 : Observed NRS and SERS bands of 3-methylpyridine

Wilson mode	Species	NRS (cm^{-1})	SERS (cm^{-1})	Enh. factor	Assignments	
m_3	-	220	224	5.0×10^4	C - CH_3	o.p.b.
-	-	-	320	-	Ag - N	str.
15	a'	340	342	4.0×10^4	C - H	i.p.b. X-sensitive
m_2	-	370	374	1.4×10^4	C - CH_3	i.p.b.
16 a	a"	394	404	5.1×10^3	C - C	c.p.b
11	a"	504	502	3.5×10^4	C - H	o.p.b.
6 a	a'	536	562	4.5×10^4	C - C	i.p.b. X-sensitive
6 b	a'	670	678	1.1×10^5	C - C	i.p.b.
4	a"	720	724	1.4×10^4	C - C	o.p.b.
10 b	a"	772	776	8.5×10^4	C - H	o.p.b.
12	a'	812	842	3.0×10^4	C - C	i.p.b. X-sensitive
10 a	a"	862	864	9.0×10^3	C - H	o.p.b.
17 a	a"	988	990	8.0×10^3	C - H	o.p.b.
1	a'	1030	1040	1.3×10^4	Ring breathing	
$M_6(b_1)$	-	1048	1058	7.5×10^3	CH_3	i.p.wag.
18 a	a'	1068	1066	5.0×10^4	C - H	i.p.b.
18 b	a'	1122	1124	4.0×10^4	C - H	i.p.b.
9 a	a'	1194	-	-	C - H	i.p.b.
$M_6(b_2)$	-	-	1150	-	CH_3	o.p.wag.
m_1	-	1240	1244	2.0×10^5	C - CH_3	str.
3	a'	-	1302	-	C - H	i.p.b.
14	a'	-	1378	-	C - C, C - N	str.
M_3	-	1400	1400	3.0×10^4	HCH sym. angle deform.	
$M_4(b_2)$	-	1430	1432	1.2×10^4	HCH assym. angle deform.	
$M_4(b_1)$	-	1442	1448	1.4×10^4	HCH assym. angle deform.	
19 a	a'	1498	1494	2.0×10^4	C - C, C - N	str.
8 b	a'	1580	1580	3.0×10^4	C - C	str.
8 a	a'	1600	1602	2.5×10^4	C - C	str.

6.3.3 4-methylpyridine

If the methyl group is considered to have cylindrical symmetry, then 4-methylpyridine (4MP) molecule has C_{2v} symmetry. The normal Raman and surface-enhanced Raman spectra of 4MP have been shown in Figs. 6.5(a) and 6.5(b) respectively. Table 6.3 contains the observed frequencies, their assignments and absolute enhancement factors. The absolute enhancement factors for various bands have been calculated as stated earlier. It has been found that the enhancement factors of the out-of-plane vibrations (species a_2 or b_1) are having higher values. The C - C out-of-plane deformation modes 16a, 4 and the C-CH_3 out-of-plane bending mode have the enhancement factors of 1.2×10^5, 2.0×10^4 and 1.5×10^4 respectively. The out-of-plane vibrations should be enhanced more if the 4MP molecules lie 'flat' on the surface of the sol particles because in that case the out-of-plane vibration will be perpendicular to the surface and it will be influenced by the surface electromagnetic field to increase the intensity [23]. This is based on the image-field effect as stated by Hexter et al [25] and King et al [26].

It is also observed that the ring breathing mode ν_1 at 1006 cm^{-1} has been red-shifted to 990 cm^{-1} in the SERS. This lowering of the ring breathing frequency signifies the formation of a bond between the ring and the sol particles [27]. Further it has been noticed that some ring vibrational modes, ν_{16a}, ν_{6a}

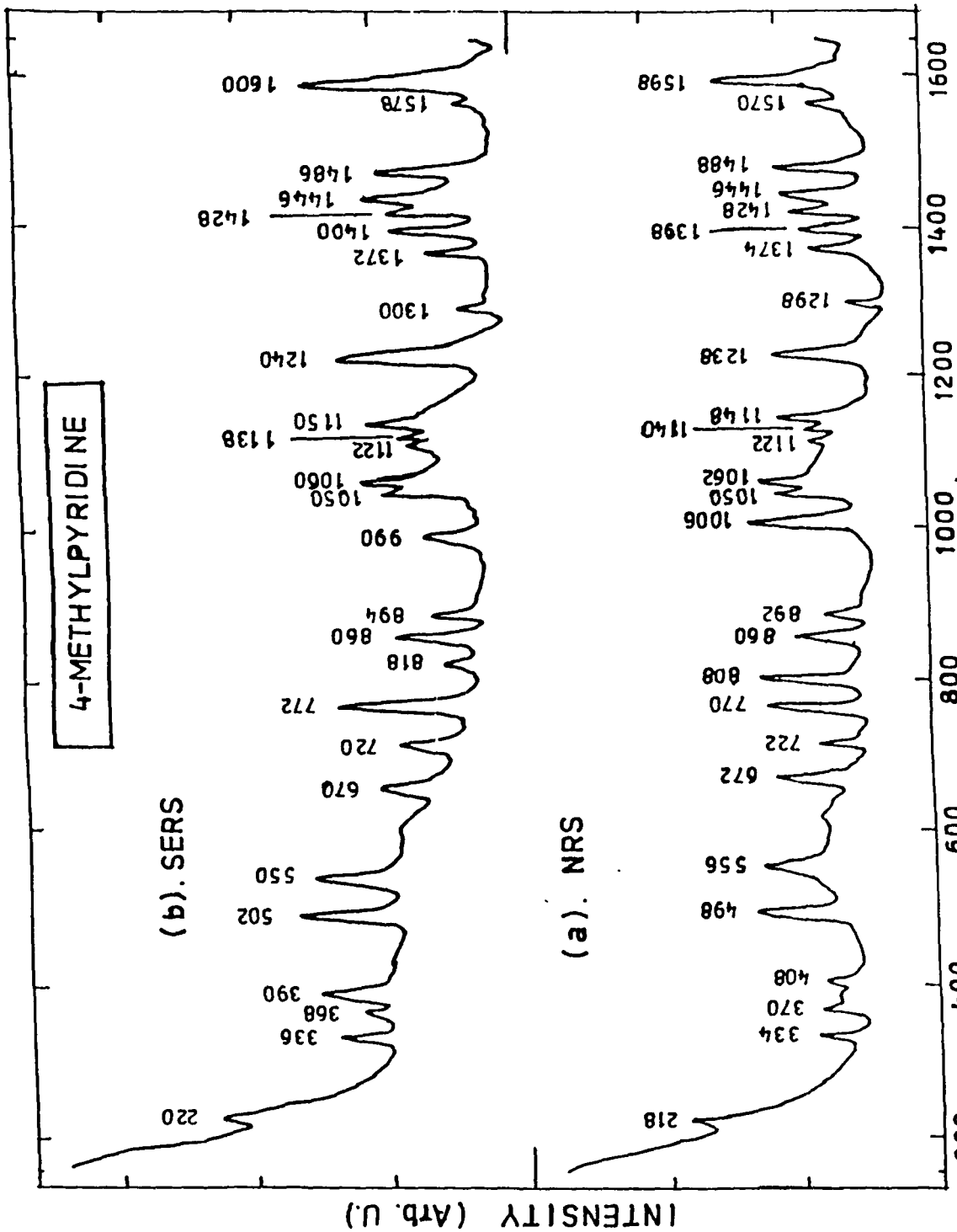

Fig. 6.5 : (a) Normal Raman Spectrum (NRS) of 4-methylpyridine solution (conc. 0.1 M)
(b) SERS spectrum of 4-methylpyridine adsorbed on silver sol (overall conc. 1.0×10^{-5}M). Laser power 100 mW (at the sample); Scan Inc. 2 cm^{-1}/step. FS CNT 3000, PMT volt 1250.

TABLE 6.3 : Observed NRS and SERS bands of 4-methylpyridine

Wilson mode	Species	NRS (cm^{-1})	SERS (cm^{-1})	Enh. factors	Assignments
m_3	-	218	220	1.5×10^4	C-CH_3 o.p.b.
15	b_2	334	336	1.4×10^4	C-H i.p.b. X-sensitive
m_2	-	370	368	1.0×10^4	C-CH_3 i.p.b.
16a	a_2	408	390	1.2×10^5	C-C o.p.b.
11	b_1	498	502	1.0×10^4	C-H- o.p.b.
6a	a_1	556	550	1.3×10^4	C-C i.p.b. X-sensitive
6b	b_2	672	670	8.0×10^3	C-C i.p.b.
4	b_1	722	720	2.0×10^4	C-C o.p.b.
10b	b_1	770	772	1.6×10^4	C-H o.p.b.
12	a_1	808	818	4.0×10^3	C-C i.p.b. X-sensitive
10a	a_2	860	860	1.8×10^4	C-H o.p.b.
5	b_1	892	894	1.3×10^4	C-H o.p.b.
1	a_1	1006	990	8.0×10^3	Ring breathing
$M_6(b_1)$	-	1050	1050	1.1×10^4	CH_3 i.p.wag.
18a	a_1	1062	1060	1.3×10^4	C-H i.p.b.
18b	b_2	1122	1122	5.0×10^3	C-H i.p.b.
9a	a_1	1140	1138	1.0×10^4	C-H i.p.b.
$M_6(b_2)$	-	1148	1150	1.2×10^4	CH_3 o.p.wag.
m_1	-	1238	1240	2.0×10^4	C-CH_3 str.
3	b_2	1298	1300	9.0×10^3	C-H i.p.b.
14	b_2	1374	1372	1.2×10^4	C-C, C-N str.
M_3	-	1398	1400	2.0×10^4	HCH Sym. ang. def.
$M_4(b_2)$	-	1428	1428	1.0×10^4	HCH asym.ang.def.
$M_4(b_1)$	-	1446	1446	1.0×10^4	HCH asym.ang.def.
19a	a_1	1488	1486	2.1×10^4	C-C, C-H str.
8b	b_2	1570	1578	8.5×10^3	C-C str.
8a	a_1^2	1598	1600	1.6×10^4	C-C str.

a) The normal Raman (NR) frequencies of the present work are comparable to the assignment of Green et al [28].

b) i.p.b. = in-plane bending, o.p.b. = out-of-plane bending, str = stretching.

are red-shifted by 18 cm^{-1} and 6 cm^{-1} respectively. This is also in favour of a strong interaction of the ring with the surface. Hence it can be concluded that the 4MP molecule has been adsorbed on the sol particles taking-up a 'flat' orientation i.e. it is lying flat on the surface making a π-bond with the surface [27]. The formation of a π- bond is preceeded by chemisorption.

6.4 CONCLUSIONS

In the present investigation, the SERS of 2-, 3- and 4-methypridines adsorbed on silver sol particles have been studied in the spectral range of 150 - 1650 cm^{-1}. The absolute enhancement of the various bands for 2MP, 3MP and 4MP molecules are in the ranges of 10^2 - 10^6, 10^3 - 10^5 and 10^3 - 10^5 respectively. The modes which got shifted are 16a, 1, 6b, 10b, 12 and m_3 (out-of-plane C-CH_3 bending) for 2MP; 12, 6a, 1, 6b and 16a for 3MP and 16a, 1, 12 and 6a for the 4MP molecules. These are accounted for the strong interaction of the surface to the relevant vibrational modes. Two possible orientations of the molecules with respect to the silver surface can be considered : 'standing-up' with binding through the lone pairs of the nitrogen atoms and 'flat' when the π-delocalized electrons of the rings interact with the colloidal particles. From the present studies, it has been demonstrated that the 4MP molecule is taking 'flat' orientation whereas the 2MP and 3MP molecules are taking 'standing-up orientation upon the surface of the silver sol

particles. It is probably because the 4-methylpyridine can delocalize more electrons into π- system via hyperconjugation than the 2- and 3-methylpyridines. The total enhancement of the bands in the SERS attributed due to both the chemical and the electromagnetic contributions. The C-CH_3 out-of-plane vibrational band has broadened more in 2MP. This may be due to the interaction of the surface as the CH_3 group is very close to the surface for standing-up orientation of the 2MP molecule. It should be mentioned that for assigning the orientation of the adsorbed molecules, the z-axis has been considered to be in the plane of the molecule and perpendicular to the surface, y-axis lies in the plane of the molecule and parallel to the surface, x-axis is perpendicular to the plane of the molecule and parallel to the surface.

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CHAPTER - VII

SURFACE ENHANCED RAMAN SCATTERING (SERS) STUDIES OF 2- and 3-CHLOROPYRIDINE ADSORBED ON SILVER HYDROSOL

7.1 INTRODUCTION

The intriguing nature of surface-enhanced Raman scattering (SERS) spectroscopy has attracted considerable attention since the recognition of a million-fold enhancement in the scattering cross sections of pyridine adsorbed on a silver electrode [1]. In recent years, SERS has been established as a useful tool in observing and investigating the structure of the adsorbed molecules and the metal-molecule interactions [2 - 5]. While an intense effort in this field concentrates on adsorbates on electrode surfaces, increased attention is presently drawn to adsorbates on colloidal particles [6 - 8]. Investigations of SERS from the molecules adsorbed on metal colloidal particles have a basic aim in understanding the fundamental nature of the enhancement mechanisms. It is now believed that there are at least two major classes of mechanisms which contribute to the overall enhancement of the Raman signals and they are (i) electromagnetic and (ii) chemical in nature.

In the electromagnetic model of SERS, the enhancement occurs because of the excitation of surface plasmons in the metal particle at both the exciting and Raman frequencies. The model has been applied only in the limits of particle size much smaller than the wavelength of the incident light, to spheroids and to coated spheres. The chemical effect deals with the interaction and bonding between the adsorbed molecule and the metal surface.

Among the various chemical effects, charge transfer (CT) interaction had attracted much attention. In this case a CT level is constructed by an unoccupied molecular orbital of the adsorbate and the electron transfer from the metal to this unoccupied molecular orbital is considered. In this paper the surface-enhanced Raman scattering (SERS) studies of 2- and 3-chloropyridine adsorbed on silver hydrosol particles have been reporded. It has been tried to establish that both the electromagnetic and the charge transfer efffects contribute to the overall enhancement of the Raman signals.

7.2 EXPERIMENTAL

7.2.1 Materials

Analytical grade silver nitrate and sodium borohydride were obtained from the Sigma chemicals U.S.A., 2-chloropyridine (Sigma, USA) and 3-chloropyridine (Aldrich,USA) were of the highest grade commercially available and was used as received. Water used for the entire work was deionized and triply distilled.

7.2.2 Preparation of Silver Hydrosol

Silver hydrosol was prepared following the method as described in ref. [6], by the reduction of silver nitrate with

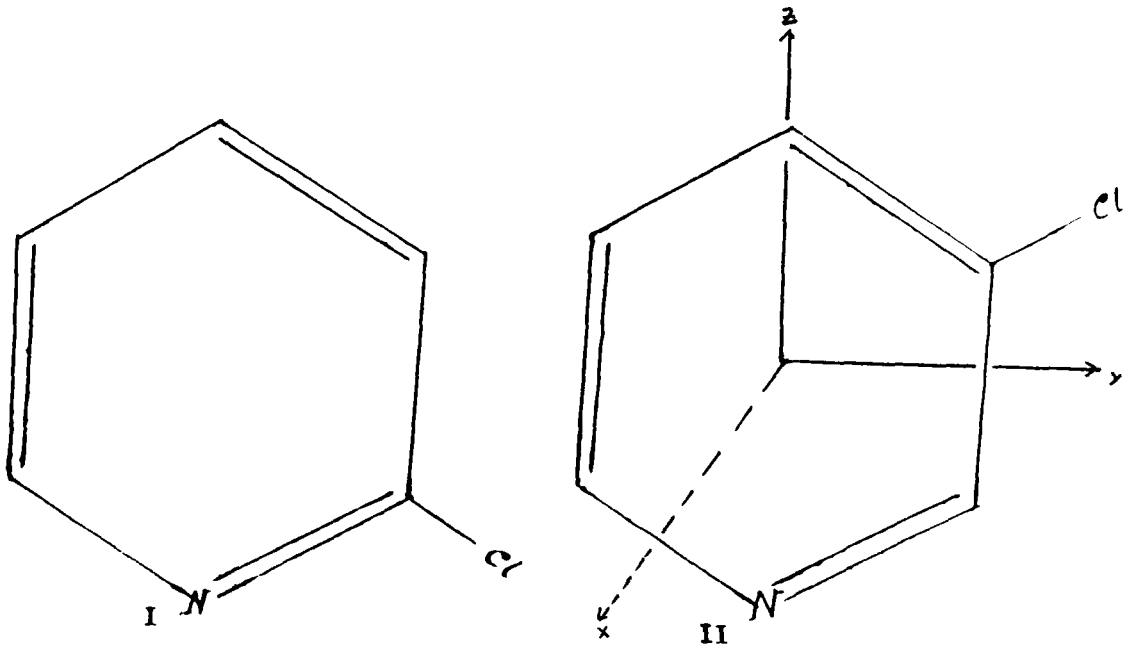

Fig. 7.1 : I Structure of 2-chloropyridine

II Structure of 3-chloropyridine

sodium borohydride. 22 ml of 1.0×10^{-3}M aqueous $AgNO_3$ solution was poured into 60 ml of 2.0×10^{-3}M aqueous solution of $NaBH_4$ under vigorous stirring. The later solution was maintained at ice-cold temperature during the preparation. A silver hydrosol with yellowish tint, thus prepared, was stable for few months. The approximate pH of the sol was measured to be in between 7 and 8.

7.2.3 Instrumentation

A RAMANOR U1000 (Jobin Yvon, France) double monochromator equipped with peltier cooled RCA/C 31034 photomultiplier tube was used to record the Raman spectra. Excitation was done with the 514.5 nm line of a Spectra Physics Model 171 Ar^+ laser operating at a laser power of 300 mW. Samples were contained in glass capillary tubes and scattered light collected 90° to the incident light. The absorption spectra of Ag sol were obtained with a Spectronic 1001 (Milton Roy, Japan) absorption spectrophotometer using cells of 1 cm thickness.

7.3 RESULTS AND DISCUSSIONS

Fig.7.2 a shows the absorption spectrum of the freshly prepared silver hydrosol. It has an extinction maxima at 396 nm which is the characteristic of the sol particles being almost

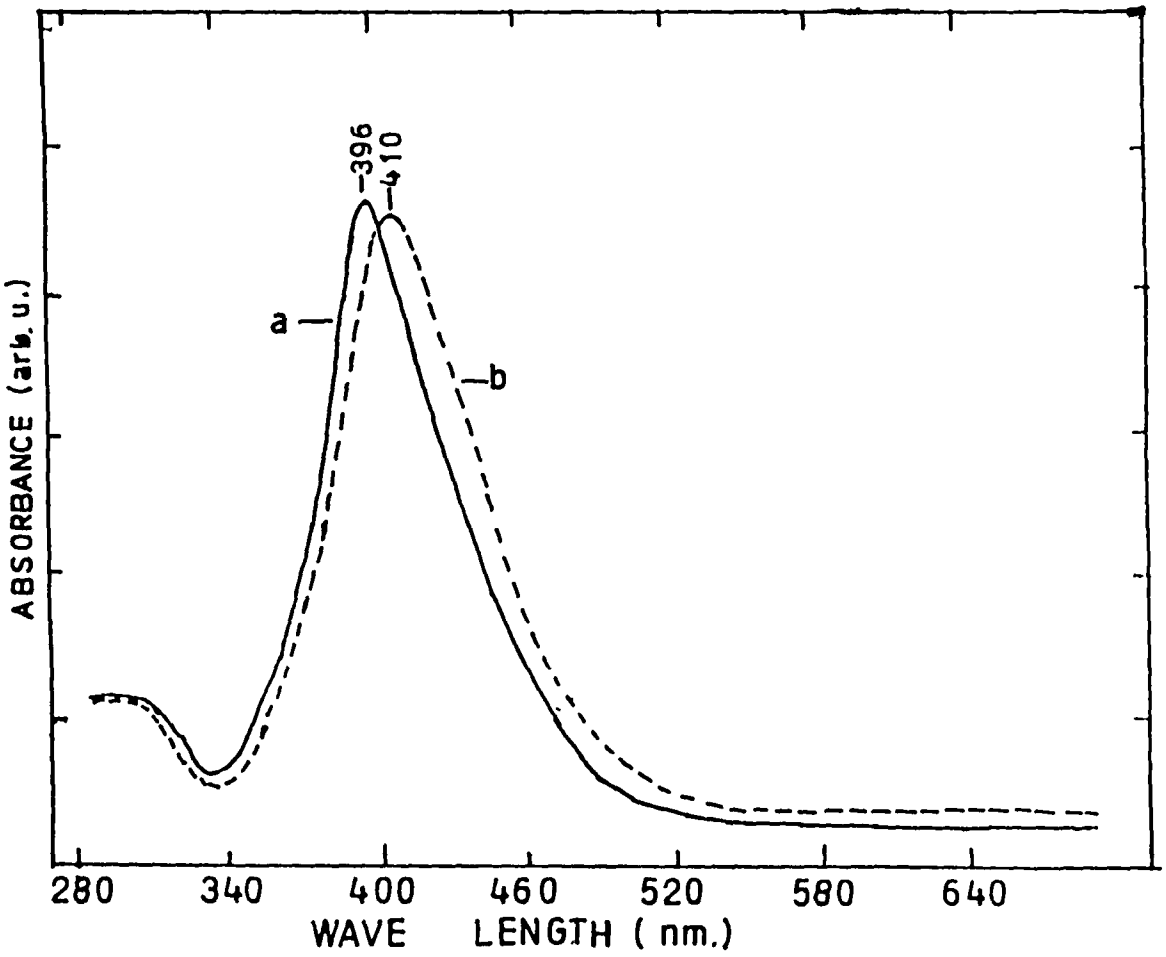

Fig. 7.2 : Absorption spectra of (a) silver sol before and (b) after addition of 2-chloropyridine.

spherical in shape with diameter in the range 1 - 50 nm [9,10]. The average diameter of the sol particles can be considered as $\approx$25 nm. Light absorption by the silver particles induces the above mentioned extinction band which is attributed to the excitation of plasma vibrations in the limited electron gas of the particles [11]. After the addition of 2- or 3-chloropyridine in the sol, its colour gets changed and the extinction band shifts to 410 nm (Fig.7.2b), which indicates the growing of the particles' size due to the small aggregation (not precipitation) of the sol particles after adsorbing chloropyridine molecules.

The normal Raman spectrum (NRS) of 2-chloropyridine (2CLP) solution (conc.0.1 M) in the spectral range of 150 - 1650 cm^{-1} has been shown in Fig 7.3(A). The surface-enhanced Raman spectrum (SERS) of 2CLP adsorbed on silver hydrosol (2CLP conc. 1.0 x 10^{-5}M) particles is shown in the Fig. 7.3(B). Table 7.1 lists the band positions, their vibrational assignments and absolute enhancement factors. The normal Raman (NR) spectrum of 2CLP at 0.1 M conc. has been compared with the SER spectrum of the same 2CLP at 1.0 x 10^{-5}M conc. as the NR bands are too weak to be observed at 1.0 x 10^{-5}M conc.

In case of 2CLP molecules , the C - C ring deformation modes ν_{16b}, ν_{6a} and ν_{12} at 180, 422 and 724 cm^{-1} have been shifted to 196, 436 and 736 respectively in SERS spectrum. These modes are blue-shifted. It has been observed that the ring

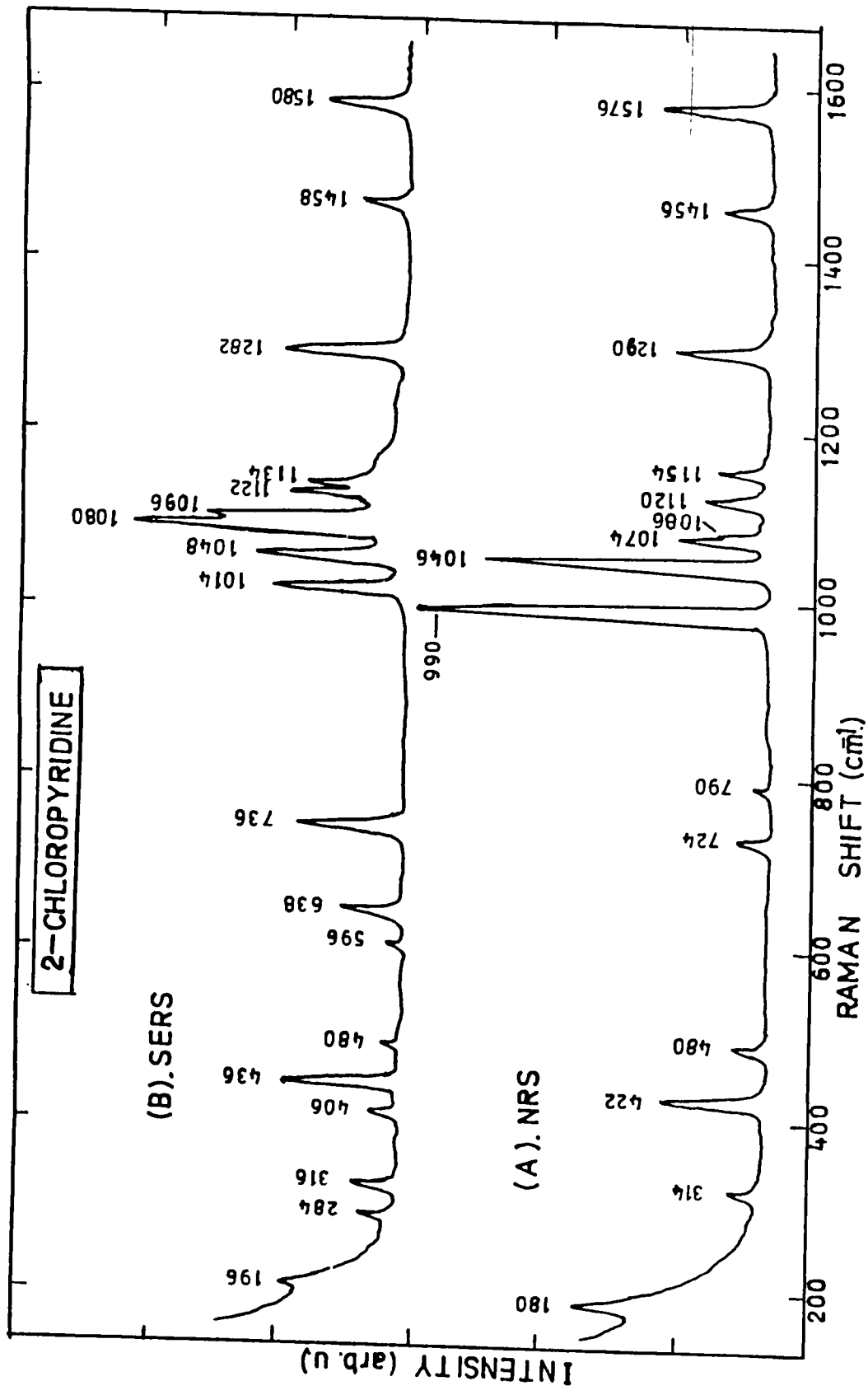

Fig. 7.3 (A) : Normal Raman spectrum (NRS) of 2-chloropyridine. Conc. 0.1M

(B) SERS spectrum of 2-chloropyridine adsorbed on silver hydrosol. Conc. 10×10^{-5} M

TABLE 7.1 : Observed frequencies (cm^{-1}), enhancement factors and assignments of bands in the NRS and SERS spectra of 2-chloropyridine

W. mode	a) NRS	SERS	En. fac.	b) Assignments
16b	180	196	8.3×10^2	a" C - C o.p.b. X- sens.
-	-	284	-	Ag - N str.
15	314	316	3.0×10^4	a' C - H i.p.b. X- sens.
16a	-	406	-	a" C - C o.p.b.
6a	422	436	1.2×10^4	a' C - C i.p.b. X- sens.
11	480	480	1.4×10^3	a" C - H o.p.b.
-	-	596	-	406 + 196 = 602 Comb.band
6b	-	638	-	a' C - C i.p.b.
12	724	730	1.1×10^5	a' C - C i.p.b. X- sens.
10b	790	-	-	a" C - H o.p.b.
1	990	1014	2.0×10^3	a' Ring breathing
18a	1048	1048	7.5×10^4	a' C - H i.p.b.
18b	1074	1080	1.3×10^6	a' C - H i.p.b.
-	1086	1096	4.0×10^5	- C - Cl str.
13	1120	1122	1.1×10^4	a' C - H str. X- sens.
9a	1154	1134	1.0×10^4	a' C - H i.p.b.
3	1290	1282	1.2×10^4	a' C - H i.p.b.
14	-	-	-	a' C - C, C - N str.
19a	1456	1458	9.0×10^3	a' C - C, C - N str.
8a	1576	1580	8.5×10^3	a' C - C str.

a) The normal Raman frequencies of the present work are comparable to the assignment of Green et al [16].

b) i.p.b. = in-plane bending, o.p.b. = out-plane bending, str = stretching

breathing mode ν_1 has been shifted to higher frequency by 24 cm^{-1} (i.e. from 990 to 1014 cm^{-1}). According to Furukawa et al [12] it is known that if the pyridine molecules are adsorbed through the ring nitrogen, the ring breathing band shifts to higher frequency. In our study we have also found the same phenomenon. So, we can assess that the 2CLP molecules have been adsorbed through the ring nitrogen atom forming a Ag-N bond. The formation of the Ag-N bond is also confirmed by the appearance of $\hat{a}^{SERS}$ band at 284 cm^{-1} which has been attributed to the Ag-N stretching mode [13].

Fig.7.4(A) and7.4(B) show the normal Raman spectrum (NRS) and SERS spectrum respectively for the 3-chloropyridine (3CLP) molecules. The frequencies of different bands, their assignments and absolute enhancement factors have been tabulated in Table 7.2 The concentration of 3CLP in solution was 0.1 M and that in hydrosol was 0.1×10^{-4}M (i.e. 1.0×10^{-5}M). It has been observed that alike 2CLP, the C - C ring bending modes ν_{16b}, ν_{6a} and ν_{12} at 182, 440 and 732 cm^{-1} have been blue-shifted except ν_{6a}. The positions of these bands in SERS are 222, 438 and 770 cm^{-1}. So, the ν_{16b} and ν_{12} have been shifted by 40 and 38 cm^{-1} respectively. We also observed, alike 2CLP, a new band at 286 cm^{-1} in the SERS spectrum which is absent in the NRS of 3CLP. By the similar arguments, as we have furnished for 2CLP, it can be concluded that the 3CLP molecules have also been adsorbed

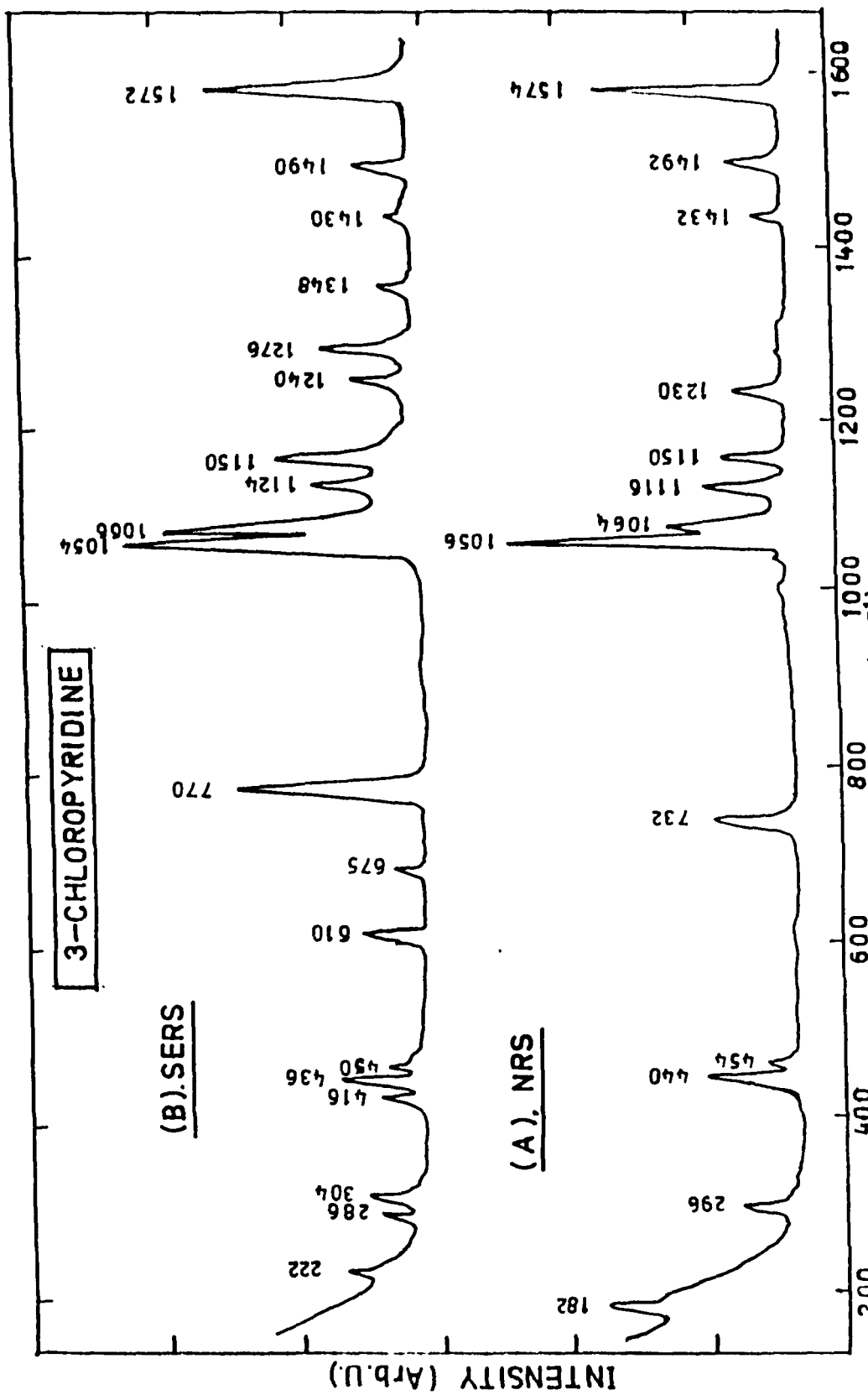

Fig. 7.4(A) : Normal Raman spectrum (NRS) of 3-chloropyridine. Conc. 0.1 M

(B) SERS spectrum of 3-chloropyridine adsorbed on silver hydrosol. Conc. 1.0×10^{-5} M

through its ring nitrogen atom forming a Ag-N bond with the silver particles.

The absolute enhancement factors of the various bands have been estimated after the method of Kerker et al [14] i.e.

$$\textbf{Abs. Enh.} = \frac{\text{Area of a particular band in SERS}}{\text{Area of the same band in NRS}} \times \frac{\text{Conc. of the sample in soln.}}{\text{Conc. of the sample in sol.}}$$

The enhancement factors for different bands of 2CLP were $10^3 - 10^6$ and for 3CLP the enhancement have been estimated $10^3 - 10^5$. It has also been found that the in-plane bending modes (species a') have been enhanced more for both in 2CLP and in 3CLP molecules whereas the out-of-plane deformation modes (species a") have been less enhanced. This also implies that the 2- and 3-chloropyridine molecules have been adsorbed through its ring nitrogen atom in the standing-up fashion. According to Creighton [15], the Raman lines whose scattering tensor elements have component perpendicular to the metal surface exhibit relatively larger intensities in the SER spectrum than those in the bulk spectrum. According to his prediction in-plane bending modes will exhibit relatively large intensity enhancement when an adsorbed molecule takes up an standing-up orientation. In the present SERS studies of 2- and 3-chloropyridine we have also observed that the in-plane modes are getting more enhanced thus supporting the standing-up orientation of the adsorbed molecule upon the surface of silver sol particle.

TABLE 7.2 : Observed frequencies (cm^{-1}), enhancement factors and assignments of bands in the NRS and SERS spectra of 3-chloropyridine.

W. mode	a) NRS	SERS	En. fac.	b) Assignments
16b	182	222	5.5×10^2	a" C - C o.p.b. X- sens.
-	-	286	-	Ag - N str.
15	296	304	1.0×10^4	a' C - H i.p.b. X- sens.
16a	-	416	-	a" C - C o.p.b.
6a	440	436	1.3×10^4	a' C - C i.p.b. X- sens.
11	454	450	5.2×10^3	a" C - H o.p.b.
6b	-	610	-	a' C - C i.p.b.
-	-	675	-	450 + 222 = 672 Comb.band
12	732	770	1.2×10^5	a' C - C i.p.b. X- sens.
18a	1056	1054	1.1×10^4	a' C - H i.p.b.
18b	1064	1066	1.1×10^5	a' C-H i.p.b./C-Cl str.
13	1116	1124	8.0×10^3	a' C - H str. X- sens.
9a	1150	1150	1.3×10^4	a' C - H i.p.b.
3	1230	1240	1.0×10^4	a' C - H i.p.b.
14	-	1276	-	a' C - C, C - N str.
-	-	1348	-	1054 + 304 = 1358 Comb.band
19b	1432	1430	5.0×10^3	A' C-C, C-N str.
19a	1492	1490	1.2×10^4	a' C - C, C - N str.
8a	1574	1572	1.3×10^4	a' C - C str.

a) The normal Raman frequencies of the present work are comparable to the assignment of Green et al [16].

b) i.p.b. = in-plane bending, o.p.b. = out-of-plane bending
str. = stretching.

7.4. CONCLUSION

The shift of band positions of some modes are attributed to the chemisorption effect. The chemisorption of a molecule on the silver surface is accompanied by an electronic transition associated with charge transfer from the metal to the molecule giving rise to a resonance effect in the Raman cross section of the adsorbed molecule. The large enhancement observed for the in-plane vibrational modes in case of standing-up orientation of the adsorbed molecule in accounted for the electromagnetic effect of SERS. So, both the chemical effect and the electromagnetic effect contribute to the overall enhancement in the SERS process. The spectral features indicate that both the 2CLP and 3CLP molecules adsorbed on the surface of silver sol particle in the standing-up position making a chemisorbed bond with the silver substrate which is also confirmed by the appearance of the Ag-N stretching band at 284 cm^{-1} and 286 cm^{-1} in the SERS spectra.

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CHAPTER - VIII

SURFACE ENHANCED RAMAN SCATTERING (SERS) STUDIES OF 2-AMINOPYRIDINE IN SILVER COLLOIDS

8.1 INTRODUCTION

The discovery of the surface-enhanced Raman scattering (SERS) by Fleischmann et al [1] has opened a wide research field both in physics and in chemistry [2,3]. SERS has played an increased role in studies of the behaviour of molecules adsorbed on metal surfaces. It allows a good Raman spectra to be obtained from a minimal quantities of the sample. Even a lower concentration of the sample down to 10^{-6} mol/litre is sufficient to record the Raman spectra. SERS has attracted considerable interest largely because of its application in the study of interfacial processes and molecular structure [3]. While an intense efforts in this field concentrates on adsorbates on electrode surfaces, increased attention is presently drawn to adsorbates on colloidal particles. Following Creighton et al's [4] observations of SERS from pyridine adsorbed on silver and gold sols, several other investigations have been performed using iron and copper sols also [5,6].

In the present study, the surface-enhanced Raman spectroscopic (SERS) investigations of 2-aminopyridine (2AP) adsorbed on silver colloidal particles have been performed. The absolute enhancement factors have been estimated to be of the order of 10^3 - 10^6 for various bands. The results have been analyzed in terms of current models for the enhancement mechanisms of SERS.

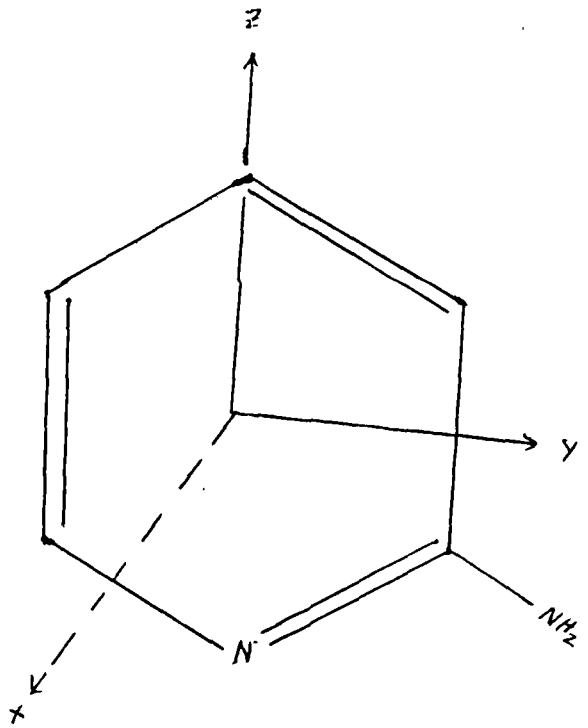

Fig. 8.1 : Structure of 2-aminopyridine molecule

8.2 EXPERIMENTAL

8.2.1 Materials

All chemicals used in this study were purchased at their highest purity commercially available. The silver nitrate, sodium borohydride and 2-aminopyridine were obtained from the Sigma Chemicals, U.S.A. Water used throughout this study was deionized and triply distilled.

8.2.2 Preparation of Colloidal Solution

The silver colloidal solution (Ag sol) have been prepared from $AgNO_3$ and $NaBH_4$ according to the procedure described as in the articles 6.2.2 and 7.2.2.

8.2.3 Instrumentation

Raman spectra were obtained with the same laser Raman spectrometer as mentioned in the previous experiments. Laser power was 200 mW. Absorption spectra of the freshly prepared colloidal solution and after addition of 2AP in the same have been recorded using the Spectronic 1001 (Milton Roy, Japan) absorption spectrophotometer. SERS spectrum was recorded 3 hours after the addition of 2AP in silver sol.

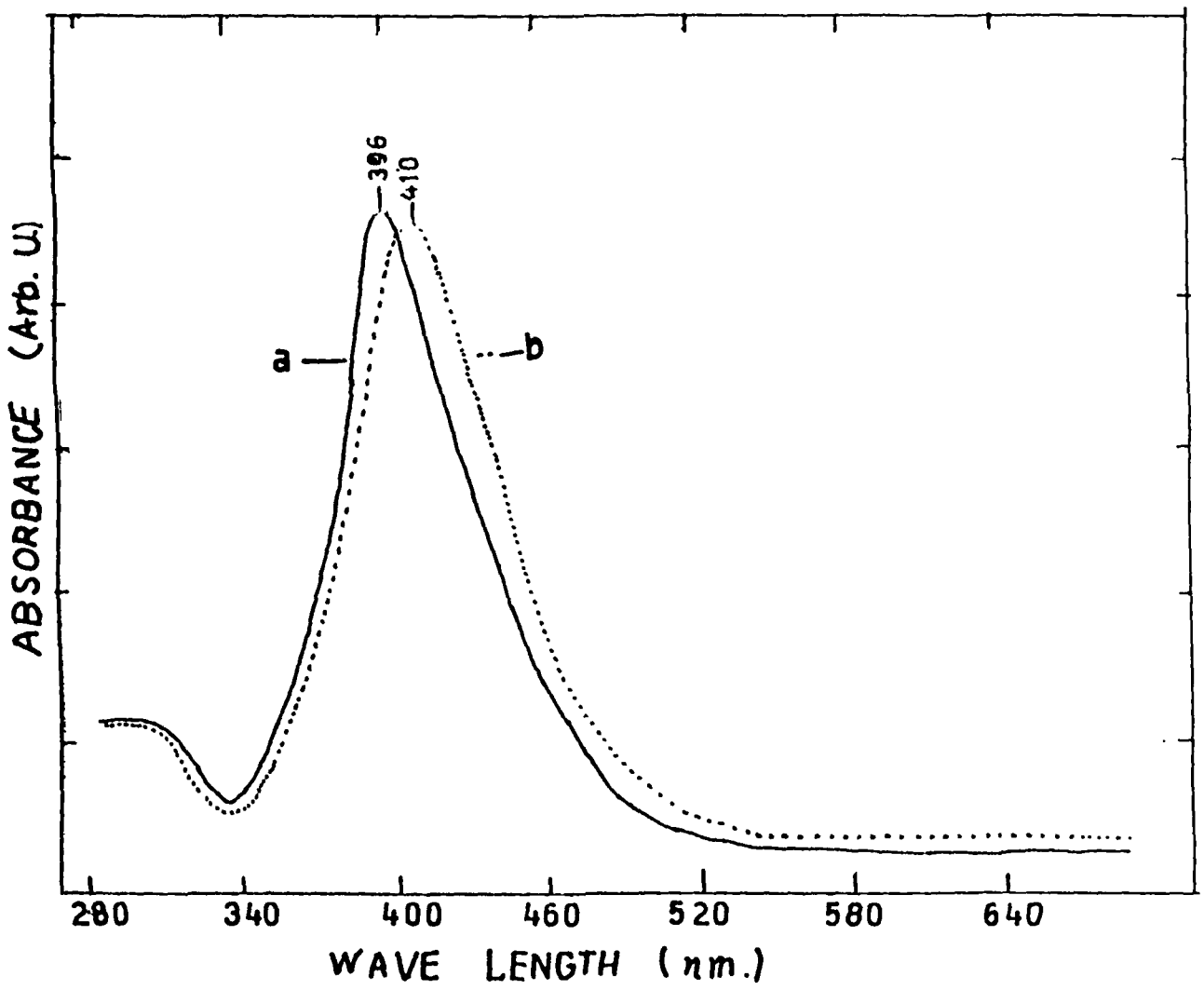

Fig. 8.2 : Absorption spectrum of (a) freshly prepared Ag sol, (b) after addition of 2-aminopyridine in the sol.

8.3 RESULTS AND DISCUSSIONS

The structure of 2-aminopyridine is shown in Fig. 8.1. The 2AP molecule is having C_s symmetry. The in-plane and out-of-plane vibrations are designated by the species a' and a" respectively. Fig. 8.2a shows the absorption spectrum of the Ag sol before addition of 2AP. It has an extinction band at 396 nm which is the characteristic of the sol particles being almost spherical in shape. The size of all the particles are not uniform. The diameter of the particles ranges from 1 - 50 nm in case of the extinction band of the sol appears near 390 nm [7,8]. After addition of 2AP in silver sol (overall 2AP conc. 1.0×10^{-4}M) the absorption spectrum was again recorded and it was found that the extinction band got shifted to the longer wavelength, at 410 nm (Fig. 8.2b). This implies that after adsorbing the 2AP molecules, the sol particles become neutral and due to the van der Waals' forces the particles aggregate and thus grow in size. Yet coagulation was not found and the sol (with 2AP) was sampled for recording the Raman spectrum.

The ordinary Raman spectrum of 2AP aqueous solution (conc. 1M) in the spectral range of 200 - 1650 cm^{-1} is shown in Fig. 8.3B. The surface-enhanced Raman spectra (SERS) of 2AP adsorbed on silver colloidal particles (2AP conc. 1.0×10^{-4}M) is shown in Fig. 8.3(A). Table 8.1 lists the band positions, their vibrational assignments and absolute enhancement factors.

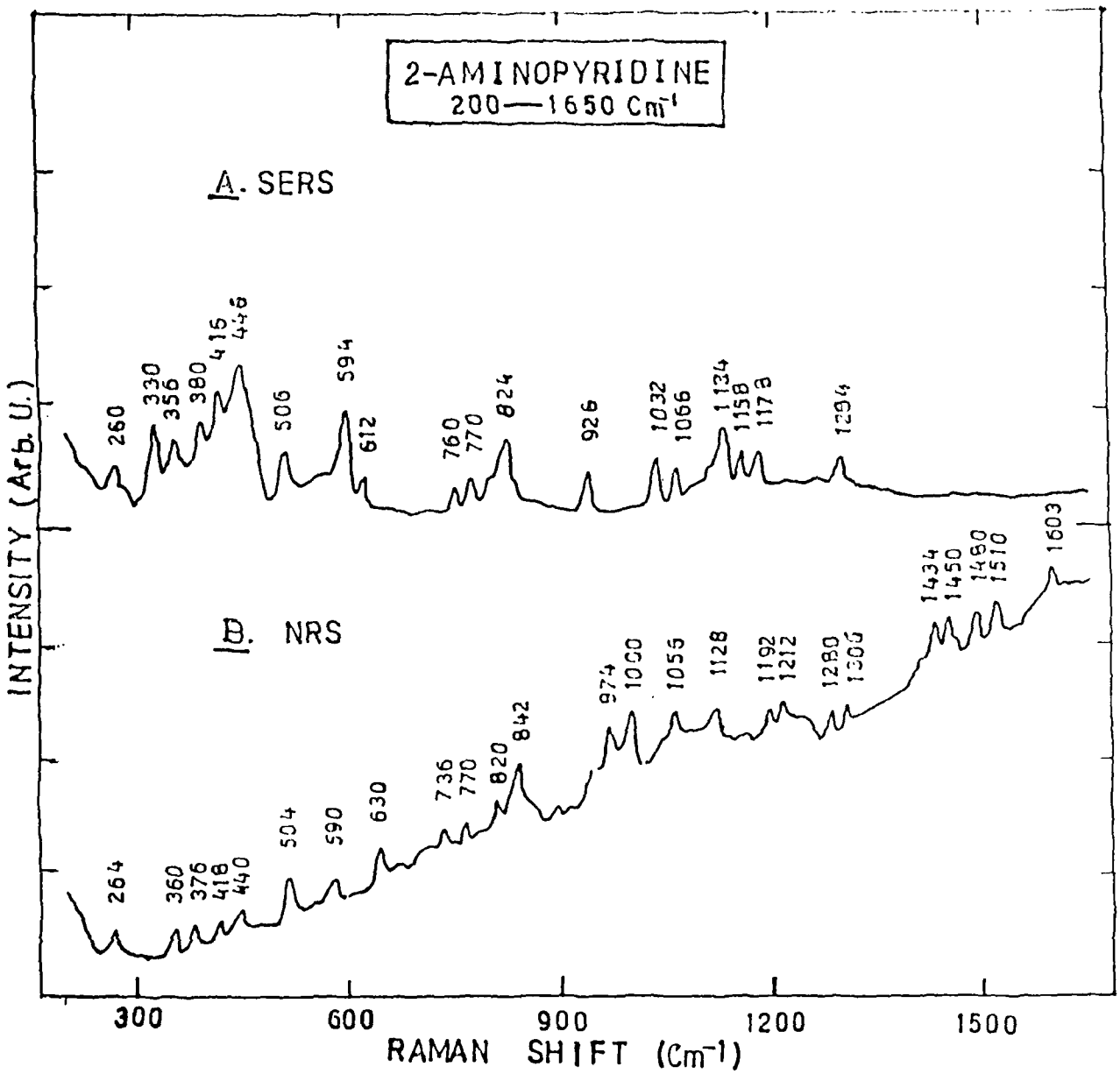

Fig. 8.3(A) : Normal Raman spectrum of 2-aminopyridine solution (conc. 1 M)

(B) : SERS spectrum of 2-aminopyridine adsorbed on silver colloidal particles (2AP conc. 1.0×10^{-4}) Laser power 200 mW, scan inc. 2 cm^{-1}/step, FS CNT 2000.

Normal Raman spectrum (NRS) of 2AP at 1M conc. have been compared with the SER spectrum of the same at 1.0×10^{-4}M conc. as the NRS bands were too weak to be observed at such lower concentration (i.e. at 1.0×10^{-4}M).

The ring deformation modes ν_{16a}, ν_{6a}, ν_{6b}, ν_4 and ν_{12} of 2AP are shifted in the SERS spectrum. From the Fig. 8.3 and Table 8.1 it is clear that the positions of those bands in NRS are 376, 590, 630 736 and 820 cm^{-1}. The SERS analogue of these bands are 380, 594, 612, 760 and 824 cm^{-1}. So, all the bands have been shifted to higher frequency except ν_{6b}. It has also been observed that the ring breathing mode has been shifted to higher frequency by 32 cm^{-1} (i.e. from 1000 to 1032 cm^{-1}). By the similar arguments as stated earlier [Articles 6.3, 7.3], it can be said that the 2AP molecule has been adsorbed through its ring N-atom which forms a bond between silver and the 2AP molecule. The formation of such bond limits the freedom of deformation of some of the modes. Thus the blue-shifting of the ring bending modes, observed in this study, is consistent with the formation of Ag-N bond. A new band has been observed at 330 cm^{-1} in the SERS spectrum which is absent in the normal Raman spectrum. This band is being assigned to Ag-N stretching vibration [9] confirms the formation of Ag-N bond. The formation of this bond arises due to chemisorption. The shift of position of some of the bands may be accounted for chemisorbed bonds.

TABLE 8.1 : Vibrational frrequencies (cm^{-1}) observed in the normal Raman and SERS spectra of 2-aminopyridine.

NRS[a]	SERS[b]	Wilson mode	Species	Abs. enh. Factor[c]	Tentative assignment[d]
264	260	-	-	1.2×10^4	C - NH_2 o.p.b.
-	330	-	-	-	Ag - N str.
360	356	15	a'	1.3×10^4	C - H i.p.b.
376	380	16a	a"	1.1×10^4	C - C o.p.b.
418	416	16b	a"	2.5×10^4	C - C o.p.b.
440	446	-		1.2×10^6	C - CH_2 i.p.b.
504	506	11	a"	1.0×10^4	C - H o.p.b.
590	594	6a	a'	8.0×10^5	C - C i.p.b.
630	612	6b	a'	6.5×10^3	C - C i.p.b.
736	760	4	a"	1.0×10^4	C - C o.p.b.
770	770	10b	a"	1.4×10^4	C - H o.p.b.
820	824	12	a'	1.0×10^6	C - C i.p.b.
842	-	10a	a"	-	C - H o.p.b.
974	926	17a	a"	1.4×10^4	C - H o.p.b.
1000	1032	1	a'	1.0×10^4	Ring Breathing
1056	1066	18a	a'	1.5×10^4	C - H i.p.b.
1128	1134	18b	a'	6.0×10^4	C - H i.p.b.
1192	1158	9a	a'	2.0×10^4	C - H i.p.b.
1212	1178	-		3.5×10^4	HNH Sym.bending
1280	1284	3	a'	1.1×10^4	C - H i.p.b.
1306	-	14	a'	-	C - C,C - N str.
1434	-	19b	a'	-	C-C, C-N str.
1450	-	-			C-NH_2 str.
1480	-	19a	a'	-	C-C, CN str.
1510	-	8b	a'	-	C-C str.
1603	-	-	-	-	HNH Assym.bend

a) 2AP conc. 1M b) 2AP conc. 1.0×10^{-4}M c) Estimated as by Kerker et al [10] d) o.p.b = out-of-plane bending, i.p.b. = in-plane bending Str = stretching, Sym = symmetric, Assym = assymetiic.

The absolute enhancement factors of different bands have been estimated as by Kerker et al [10]. The maximum enhancement factors have been observed for the in-plane bending modes. The C-NH_2 in-plane bending (i.e. aromatic ring-NH_2 bending) mode at 440 cm^{-1} and C-C in-plane modes at 590 and 820 cm^{-1} have been enhanced upto the order of 1.2×10^6, 8.1×10^5 and 1.0×10^6 respectively. Creighton [11] had emphasized that, due to the electromagnetic effect Raman lines whose scattering tensor elements have components perpendicular to the metal surface exhibit relatively larger intensities in the SER spectrum than those in the bulk. According to this prediction, in-plane bending modes will exhibit relatively large intensity enhancement when an adsorbed molecule takes-up an edge-on (i.e. standing-up) orientation. In the present study it has been found that the in-plane modes are getting more enhanced and thus supporting the standing-up orientation of the adsorbed molecule.

8.4 CONCLUSION

The spectral features indicate that the SERS spectrum is having less background whereas the NRS is having more background. It has been established, that the 2AP molecule have been adsorbed on the surface of silver sol particle in the edge-on (i.e. standing-up) postion making a chemisorbed bond with the silver substrate which is also confirmed by the appearance

of the Ag-N stretching band in the SERS spectrum. This is further in agreement with the observed enhancement factor which corresponds to Creighton's surface selection rules. The role of both chemical and electromagnetic effects have been observed to contribute in the overall enhancement in the SERS phenomenon.

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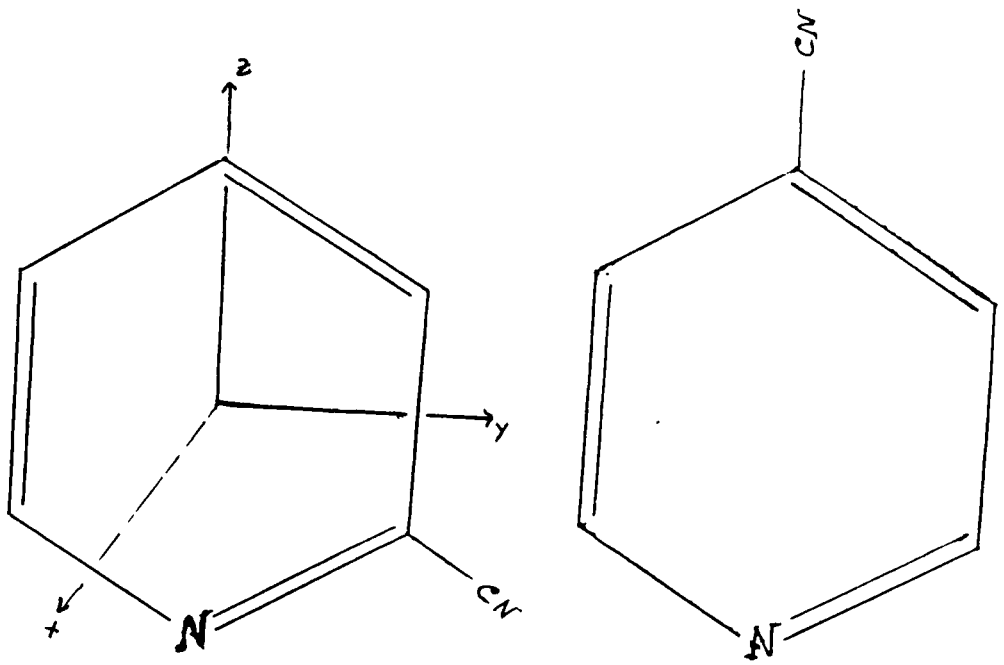
CHAPTER - IX

SURFACE ENHANCED RAMAN SCATTERING (SERS) STUDIES OF 2- and 4-CYANOPYRIDINE ADSORBED ON SILVER SOL

9.1 INTRODUCTION

Surface-enhanced Raman Scattering (SERS) is a useful technique for the study of molecular adsorption on metal surfaces. Especially, information of the adsorbed species and its structure can be obtained from the SERS spectra. Fleischmann et al [1] were the first to record the SERS spectra of adsorbed species from high surface area electrode. They investigated pyridine spectra adsorbed on a silver electrode that had been roughened by electrochemical oxidation-reduction process. Since then SERS of molecules adsorbed on rough noble-metal surfaces has been extensively studied both experimentally and theoretically [2,3,4]. Creighton [5] and his co-workers were the pioneer in investigating SERS of pyridine in colloidal particles. Afterwards, many investigations have been performed using silver, gold, iron and copper sol [6,7,8].

The surface-enhanced Raman scattering (SERS) of cyanopyridines adsorbed on electrode surface was investigated by Allen and van Duyne [9]. They studied the competetive adsorption of cyanopyridines on silver electrode surface. SERS of 4-cyanopyridine has been reported by Furukawa et al [10], Rubim [11] and Muniz-Miranda et al [12]. All these investigations were performed on electrode surfaces. In the present work, the SERS of 2- and 4-cyanopyridines have been investigated using silver colloidal solution. Allen and



I II

Fig. 9.1 : I. Structure of 2-cyanopyridine; II. Structure of 4-cyanopyridine molecule.

van Duyne [9] have specified the orientation of the adsorbed cyanopyridine molecules on the electrode surface by comparing the enhancement factor of the C≡N stretching mode with respect to the ring breathing mode. In the present work we have estimated the absolute enhancement factors for all the bands as well as their shifting in frequencies and thus tried to make a propensity rule for the orientation of the adsorbed molecule.

9.2 EXPERIMENTAL

9.2.1 Materials and colloid preparation

$AgNO_3$ (British Drug House), $NaBH_4$ (Ubichem, U.K.) and 2-cyanopyridine (Sigma Chemicals, U.S.A) and 4-cyanopyridine (Fluka) were of highest purity commercially available and were used as received. Water was deionized and triply distilled. The silver colloidal solution was prepared according to the procedure described by Creighton et al [5]. Briefly, a 1.0×10^{-3}M aqueous solution of $AgNO_3$ was mixed with 2.0×10^{-3}M aqueous solution of $NaBH_4$ in the volume ration 1 : 3. $NaBH_4$ solution was maintained at ice-temperature and the mixture was stirred vigorously during the preparation of colloidal solution. A yellowish coloured silver colloidal solution thus prepared was stable for a few months without any stabilizing agent. The pH of the colloidal solution was in between 7 and 8.

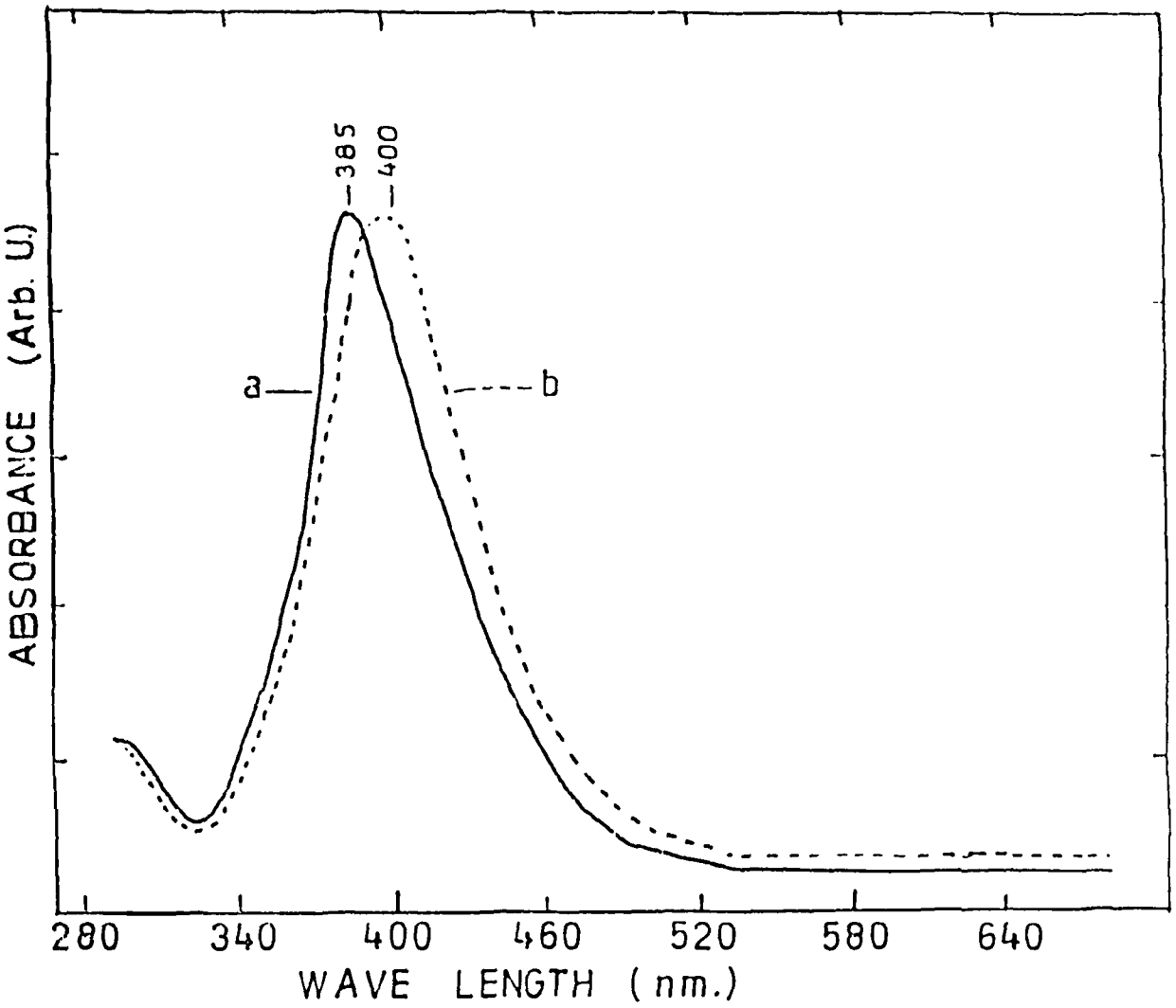


Fig. 9.2 : Extinction spectra of (a) freshly prepared silver sol (b) after addition of 2-cyanopyridine in silver sol.

9.2.2 Instrumentation

The UV/visible extinction spectra of the colloidal solution and the Raman spectra were recorded in the same procedure as reported in the previous experiments [Art. 6.2, 7.2, 8.2]. The laser power was 300 mW (not at the sample).

9.3 RESULTS AND DISCUSSIONS

Fig. 9.1 shows the structure of 2- and 4-cyanopyridine molecules. The 2-cyanopyridine (2CP) molecule is having C_s symmetry whereas the 4-cyanopyridine (4CP) molecule possesses the C_{2v} symmetry. Fig. 9.2(a) is the extinction spectrum of silver colloidal solution. Only one single extinction band near 385 nm has been observed which is an indication of the particle size being about 1-50 nm [13]. The absorption spectrum has also recorded after the addition of 2CP in the same sol [Fig. 9.2(b)]. In the second case the single extinction band was shifted to 400 nm which is an indication of growing particles' size due to adsorption [7,14]. The absorption spectrum of the silver sol has also recorded after the addition of 4CP in the silver sol. In the later case the extinction band was at 402 nm.

9.3.1 2-Cyanopyridine (2CP)

Fig. 9.3(a) shows the normal Raman (NR) spectrum of 0.75 M aqueous 2CP solution. Fig. 9.3(b) is the SERS spectrum

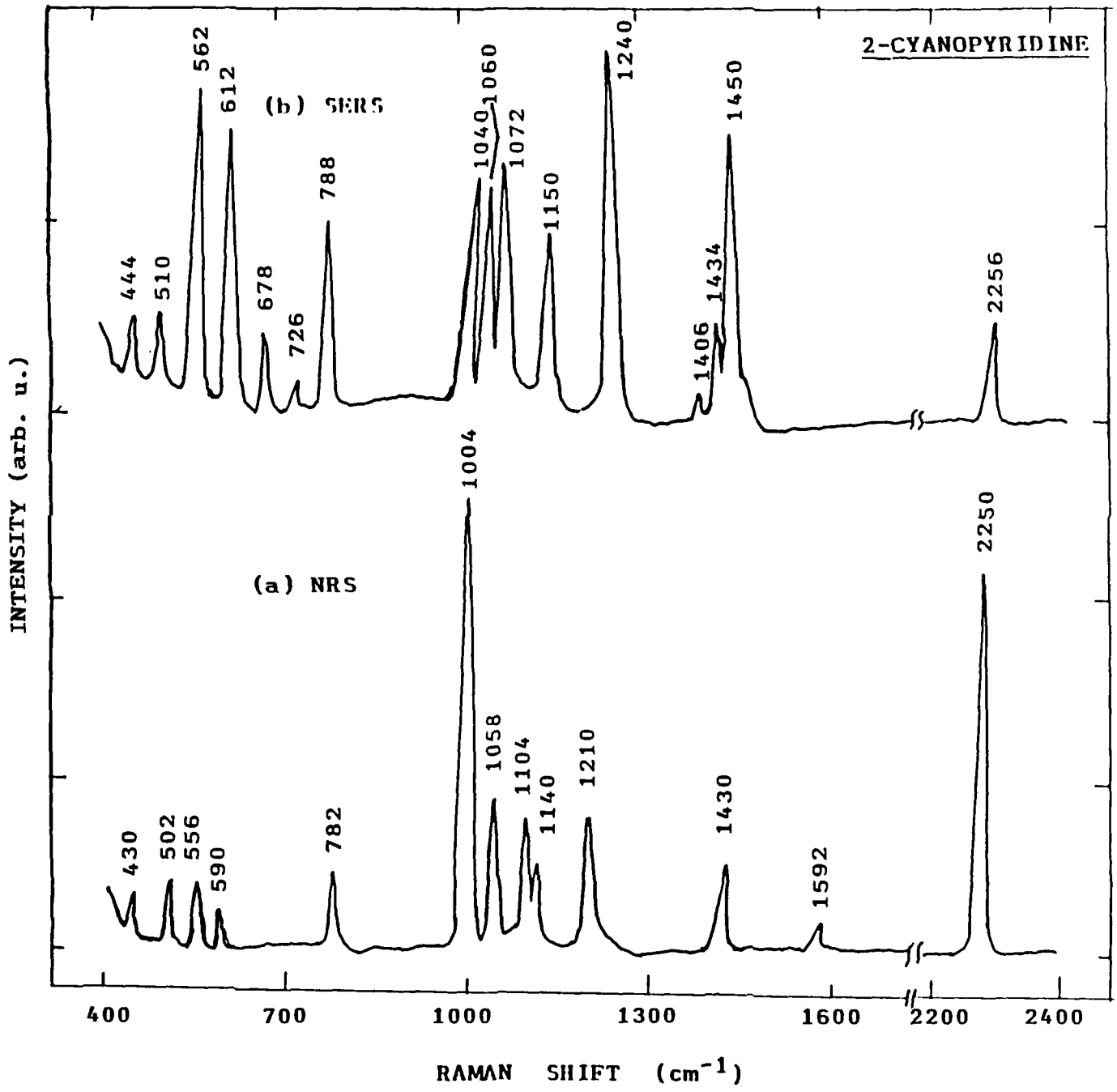


Fig. 9.3(a): Normal Raman spectrum of 2CP. Laser Power 300 mW. Scan Inc. 2 cm^{-1}/step, FS CNT 3000.

(b) SERS of 2CP, Laser Power 300 mW. Scan Inc. 2 cm^{-1}/step, FS CNT 3000.

of 2CP with colloidal solution in which the concentration of 2CP was 7.5×10^{-5}M. The NR spectrum of 2CP solution at 7.5×10^{-5}M conc. was not possible to record due to weak signals but the SERS spectrum of the same at such lower concentration was possible. So, NR spectrum of 2CP at 0.75 M conc. has been compared with the SERS spectrum of 2CP at 7.5×10^{-5}M conc. The NRS bands at 430, 502, 556, 590, 782, 1004, 1058, 1104, 1140, 1210, 1430 and 2250 cm^{-1} correspond to the SERS bands at 444, 510, 562, 612, 788, 1040, 1060, 1072, 1150, 1240, 1434 and 2256 cm^{-1} respectively. All the band frequencies, their tentative assignments along with their absolute enhancement factors have been tabulated in Table 9.1.

The C - C bending modes 16a, 6a, 6b and 12 at 430, 556, 590 and 782 cm^{-1} in the NRS have been shifted to higher frequencies at 444, 562, 612 and 788 cm^{-1} respectively in the SERS spectrum. The ring breathing mode has been shifted from 1004 cm^{-1} to 1040 cm^{-1}. These shifts towards the higher frequencies imply the formation of a bond between the Ag surface and the ring N-atom [10]. The formation of such bond (Ag-N) limits the freedom of deformation of some of the modes and thus the frequencies of those modes shift towards the higher values. The enhancement factors of in-plane bending modes 6a and 6b are found maximum. These modes belong to a' species. All the modes of a" species are less enhanced. The large enhancement

TABLE 9.1 : Vibrational frequencies (cm^{-1}) observed in the normal Raman (NR) and SERS spectra of 2-cyanopyridine.

NRS[a] (cm^{-1})	SERS[b] (cm^{-1})	Abs. Enh[c]	Assignment		
			Species (C_s)	Description of modes	Wilson No.
430	444	1.2×10^2	a"	C-C o.p.b.	16a
502	510	2.2×10^3	a"	C-H o.p.b.	11
556	562	1.3×10^5	a'	C-C i.p.b	6a
590	612	1.2×10^5	a'	C-C i.p.b.	6b
-	678	-	-	-	-
-	726	-	a"	C-C o.p.b.	4
782	788	3.0×10^4	a'	C-C i.p.b.	12
1004	1040	5.6×10^3	a'	C-C ring br.	1
1058	1060	4.0×10^4	a'	C-H i.p.b.	18a
1104	1072	2.0×10^4	a'	C-H i.p.b.	18b
1140	1150	2.8×10^4	a'	C-H i.p.b.	9a
1210	1240	4.7×10^4	a'	C-H stretch	13
-	1406	-	-	678+726=1404	-
1430	1434	3.5×10^4	a'	C-C,C-N str.	19b
-	1450	-	a'	C-C,C-N str.	19a
1592	-	-	a'	C-C stretch	8a
2250	2256	2.0×10^2	a'	C N stretch	-

a) 2CP conc. was 0.75 M

b) 2CP conc. was 7.5×10^{-5} M

c) estimated as by Kerker et al's [20] method

i.p.b = in-plane-bending, o.p.b = out-of-plane bending

str = stretch, br. = breathing.

of a' modes imply the standing-up orientation of the adsorbed 2CP molecule on the sol particle [15]. King et al [16] suggested that stronger signals are observed for vibrations which generate a large image field. As a vibration perpendicular to a metal surface generates a large image field, the signals of in-plane bending vibrations (species a') should be enhanced more if the molecules are adsorbed on the silver particles in standing-up fashion, as observed in the present study. The C - C out-of-plane band at 726 cm^{-1} is active only in IR [17] but in the present study the same band has been observed in the SERS spectrum. This implies that the Raman selection rules are not being strictly followed in the SERS spectrum. The relaxation of the Raman selection rule has also been established by Muniz-Miranda et al [12] in the SERS of pyrazine. The band at 678 cm^{-1} may be due to a complex formed by the adsorbed species with the silver substrate. The band at 1406 cm^{-1} is a combination of 678 and 726 cm^{-1} bands. The appearance of combination band in SERS has also been predicted by Takahashi et al [18]. The band at 1450 cm^{-1} is too weak to be observed in the NRS of 2CP at 0.75 M conc. but the same band comes out in the SERS spectrum with considerable intensity.

9.3.2 **4-Cyanopyridine (4CP)**

Normal Raman spectrum of 0.75 M aqueous 4CP solution has been shown in Fig. 9.4a, whereas Fig. 9.4b is the SERS

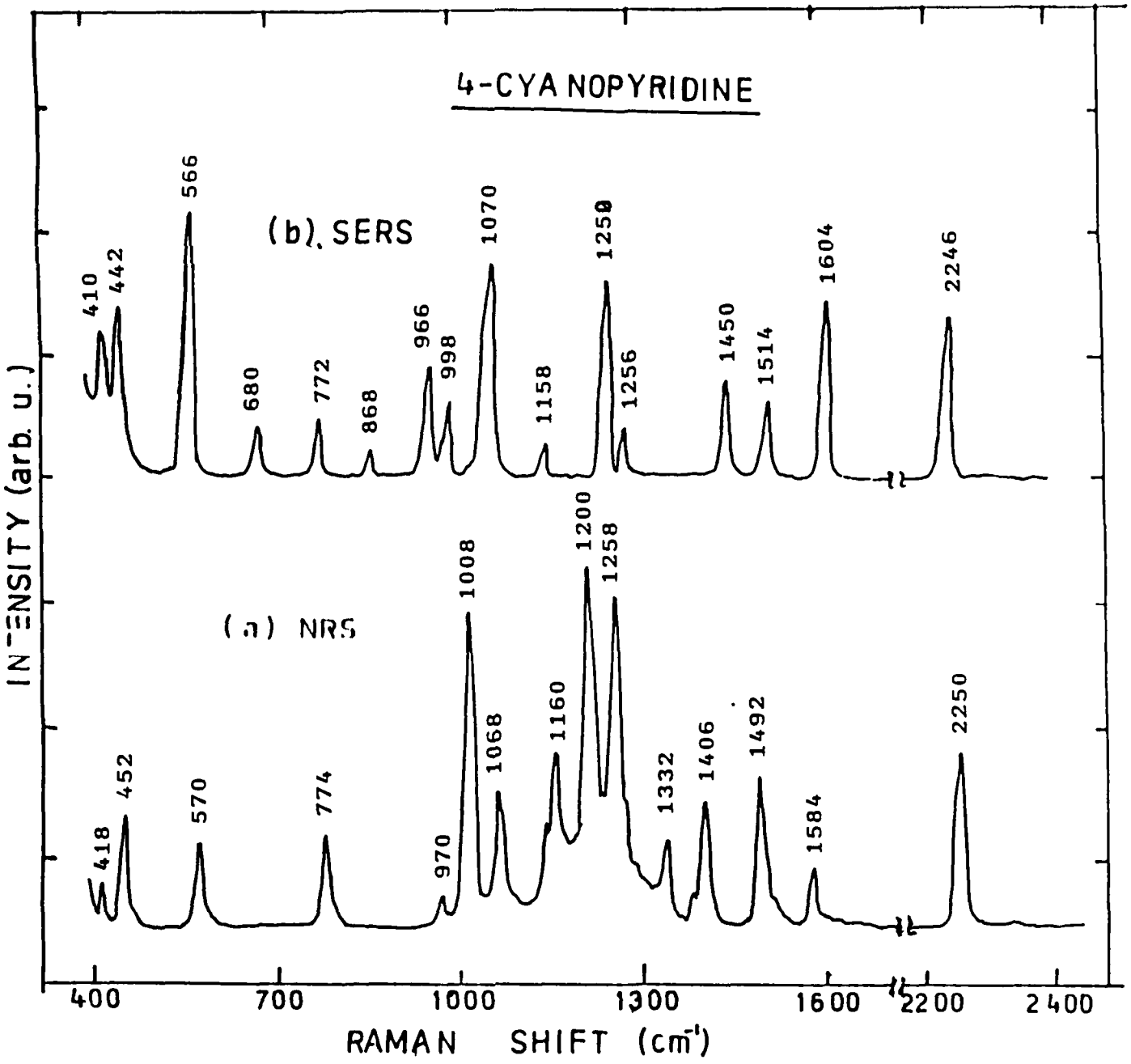


Fig. 9.4(a) : Normal Raman spectrum of 4CP. Laser Power 300 mW. Scan Inc. 2 cm^{-1}/step, FS CNT 3000.

(b) SERS of 4CP, Laser Power 300 mW. Scan Inc. 2 cm^{-1}/step, FS CNT 3000.

spectrum of 4CP with silver sol in which the overall concentration of 4CP was only 7.5×10^{-5}M. The NR bands at 418, 452, 570, 774, 970, 1008, 1068, 1160, 1258, 1406, 1492, 1584 and 2250 cm^{-1} correlate with the SERS bands at 410, 442, 566, 772, 966, 998, 1070, 1158, 1256, 1450, 1514, 1604 and 2246 cm^{-1} respectively. Table 9.2 lists the band frequencies, their assignments and enhancement factors. It has been observed that the out-of-plane bending modes (species a_2) at 418 and 970 cm^{-1} have been enhanced more (enhancement factors being 3.5×10^5, and 1.2×10^5 respectively). The large enhancement of the out-of-plane modes [species a_2 (xy)] signify that the 4CP molecule takes-up 'flat' orientation after being adsorbed on the silver colloidal particles [15]. The ring breathing mode at 1008 cm^{-1} has been red-shifted to 998 cm^{-1}. Similarly, the C - C ring bending modes at 418, 452, 570 and 774 have been red-shifted (i.e. shifted towards the lower frequency). Red-shift of the ring bending and ring breathing modes imply the flat orientation of the molecule on the surface of the particle forming a π-bond between the ring and the Ag-surface [19]. The SERS band at 1250 cm^{-1} has been assigned to be acombination of 566 and 680 cm^{-1} bands. The appearance of combination band in SERS is possible as mentioned before.

TABLE 9.2 : Vibrational frequencies (cm^{-1}) observed in the normal Raman (NR) and SERS spectra of 4-cyanopyridine

NRS[a] (cm^{-1})	SERS[b] (cm^{-1})	Abs. Enh[c]	Assignment		
			Species (C_s)	Description of modes	Wilson No.
418	410	3.5×10^5	a_2	C-C o.p.b.	16a
452	442	5.0×10^4	a_1	C-C i.p.b.	6a
570	566	1.0×10^5	b_1	C-H o.p.b	11
-	680	-	b_2	C-C i.p.b	6b
774	772	5.4×10^3	a_1	C-C i.p.b.	12
-	868	-	b_1	C-H o.p.b.	5
970	966	1.2×10^5	a_2	C-H o.p.b.	17a
1008	998	2.0×10^3	a_1	C-C ring breath.	1
1068	1070	6.3×10^4	b_2	C-H i.p.b.	18a
1160	1158	4.0×10^2	a_1	C-H i.p.b.	18b
1200	-	-	a_1	C-H stretch	9a
-	1250	-	-	566+680=1246	comb. band
1258	1256	5.0×10^3	a_1	C-H stretch	13
1332	-	-	b_2	C-H i.p.b.	14
1406	1450	7.6×10^3	b_2	C-C,C-N stretch	19b
1492	1514	6.0×10^3	a_1	C-C,C-N stretch	19a
1584	1604	5.0×10^3	b_2	C-C stretch	8a
2250	2246	9.0×10^3	a_1	C ≡ N stretch	-

a) 4CP conc. was 0.75M b) 4CP conc. was 7.5×10^{-5}M

c) estimated as by Kerker et al's [20] method

i.p.b = in-plane-bending, o.p.b = out-of-plane bending

9.4 CONCLUSIONS

In the present studies, the ordinary Raman and surface-enhanced Raman spectra of 2- and 4-cyanopyridines have been investigated in the spectral range of 400 - 2400 cm^{-1}. The absolute enhancement factors of the different bands have been estimated to be in the range of 10^2 - 10^5 for both the molecules. The 2CP molecule is taking-up edge-on (i.e. standing-up) orientation on the silver surface whereas the 4CP molecules seem to be adsorbed on the surface by taking-up the flat orientation. The C ≡ N stretching vibration (at 2246 cm^{-1}) of the adsorbed 4CP molecule has been appeared with considerable enhancement though the same band is weak in case of adsorbed 2CP molecules. So, the C ≡ N (i.e. nitrile) stretching vibration in SERS is dependent on its position. The more is the CN group away from the ring nitrogen, the more is the enhancement. The shifts of band positions of different modes may be attributed to the charge-transfer effect as described in the previous experiments [21]. The large enhancement of out-of-plane vibrations in case of flat orientation and the large enhancement of the in-plane vibrations in case of standing-up orientation may be attributed to the electromagnetic effects of SERS. In the present studies it has been observed that the SERS can relax the Raman selection rules.

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INFERENCES

In the present investigations, the SERS of 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 2-chloropyridine, 3-chloropyridine 2-aminopyridine, 2-cyanopyridine and 4-cyanopyridine have been carried out in silver colloidal solution. A summary of the study may be furnished in the following tabular form :

Molecules	Sym.	Species which getting more enhanced	Nature of shift of modes	Orientation of the adsorbed molecules
2-methylpyridine	C_s	a'; in-plane bending modes	Ring breathing mode blue-shifted, ring bending modes blue-shifted	Standing-up
3-methylpyridine	C_s	a'; in-plane bending modes	Ring breathing mode blue-shifted, ring bending modes blue-shifted	Standing-up
4-methylpyridine	C_{2v}	a_2,b_1; out-of-plane bending modes	Ring breathing mode red-shifted, ring bending modes red-shifted	Flat
2-chloropyridine	C_s	a'; in-plane bending modes	Ring breathing mode blue-shifted, ring bending modes blue-shifted	Standing-up
3-chloropyridine	C_s	a'; in-plane bending modes	Ring breathing mode blue-shifted, ring bending modes blue-shifted	Standing-up
2-aminopyridine	C_s	a'; in-plane bending modes	Ring breathing mode blue-shifted, ring bending modes blue-shifted	Standing-up
2-cyanopyridine	C_s	a'; in-plane bending modes	Ring breathing mode blue-shifted, ring bending modes blue-shifted	Standing-up
4-cyanopyridine	C_{2v}	a_2,b_1; out-of-plane bending	Ring breathing mode red-shifted, ring bending modes red-shifted	Standing-up

It should be mentioned that for assigning the orientation of the adsorbed molecules, the z-axis has been considered to be in the plane of the molecule and perpendicular to the surface, y-axis lies in the plane of the molecule and parallel to the surface, x-axis is perpendicular to the plane of the molecule and parallel to the surface.

From the summary Table, a propensity rule can be drawn; pyridine derivatives having their substituents at the 2- or 3-positions (C_s symmetry) are getting adsorbed in the standing-up (i.e. plane of the molecule perpendicular to the surface) orientation whereas the derivatives having their substituents in the 4-position (C_{2v} symmetry) are taking up flat orientation on the surface of the silver sol particles. It is probably because the 4-positioned derivatives can delocalize more electrons into π- system via hyperconjugation than the 2- or 3- positioned derivatives.

LIST OF FIGURES

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